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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

Tablets of detergent composition are compacted to a diametral fracture stress of 8 to 60 KPa using mould parts at least one of which bears an elastomeric layer to contact the composition. This enhances permeability at the tablet surface and hence the speed of water uptake and speed of dissolution/disintegration at the time of use.

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# DETERGENT COMPOSITIONS

The invention relates to detergent compositions in the form of tablets, for use in fabric washing.

Detergent compositions in tablet form are described, for example, in GB 911204 (Unilever) and US 3953350 (Kao). They are sold commercially in Spain. Tablets have several advantages over powdered products: they do not require measuring and are thus easier to handle and dispense into the washload, and they are more compact, hence facilitating more economical storage. These detergent tablets are intended to be consumed completely when washing a single load. Thus they should disperse/dissolve completely when added to water.

Detergent tablets are generally made by compressing or compacting a detergent powder, which includes detergent active and detergency builder. It is desirable that tablets have adequate strength when dry, yet disperse and dissolve quickly when added to wash water.

Such tablets can be manufactured by stamping a chosen quantity of the detergent composition using a press with steel dies (also referred to as punches) which contact the powder and apply pressure so as to compact the powder into a tablet. Such a press may for example have two dies which move together within a surrounding sleeve, or one die which is driven towards a fixed anvil, again within a surrounding sleeve.

When making tablets, with any kind of material not necessarily detergent, a problem which can arise is adhesion of the composition to the steel mould parts. Adhesion of material to mould parts is disadvantageous, because the accumulated material spoils the surface finish of articles compacted in the mould. The traditional approaches to this problem have been to provide a low friction surface on the mould parts, e.g. a conventional non-stick coating of polytetrafluoroethylene, or else to apply a release agent, for example magnesium stearate.

US-A-3081267 teaches that the dies should rotate relative to each other while compressing the composition, so as to prevent the composition from adhering to them.

GB-A-2276345 teaches the stamping of articles, including tablets of compacted detergent powder, using mould parts surfaced with an elastomeric material of some thickness. This is stated to reduce unwanted adhesion to mould parts provided that the elastomer-surfaced mould exhibits a suitable overall modulus of elasticity. The document explains that a suitable modulus of elasticity can be achieved with a surface coating of elastomer which is at least 0.5mm thick. A range of 0.5 to 7mm is disclosed.

The thicknesses which are exemplified are about 4mm.

In WO 97/20028 published in June 1997, we have disclosed the stamping of tablets using dies which carry a thin elastomer coating, which has a thickness not exceeding 0.5mm over much or all of its area. This overcomes the problem of adhesion to the dies, and produces tablets, with a smooth surface.

By contrast, by using dies which carry a thicker elastomer coating, we have found that the penetration of water into the tablets on immersion is increased, thereby accelerating the dispersion/dissolution of the tablets at the time of use.

Therefore, in one aspect, the present invention provides the use of an elastomeric layer, more than 0.5mm thick, on a surface area of at least one mould part in a press for compacting particulate detergent composition into tablet form, which surface area contacts the composition during compaction;

in order to enhance the penetration of water through the tablet surface on immersion.

It is envisaged that the use of such an elastomeric layer will in particular be applied to the compaction of particulate detergent compositions having a bulk density of at least 650g/litre. Starting from a particulate composition of relatively high bulk density diminishes void space within particles relative to void space between particles. This is desirable because inter-particle porosity is more accessible to water on immersion.

The step of compacting the particles reduces the porosity of the composition. Porosity is conveniently expressed as the percentage of volume which is air.

The air content of a tablet can be calculated from the volume and weight of the tablet, provided the air-free density of the solid content is known. The latter can be measured by compressing a sample of the material under vacuum with a very high applied force, then measuring the weight and volume of the resulting solid.

The percentage air content of the tablet varies inversely with the pressure applied to compact the composition into tablets while the strength of the tablets varies with the pressure applied to compact them into tablets. Thus the greater the compaction pressure, the stronger the tablets but the smaller the air volume within them.

We have preferred to make tablets with a cylindrical shape in which the height of the cylinder is generally less than its diameter. A test of the strength of such tablets is the diametral fracture stress (DFS) determined using a testing machine which can urge a pair of confronting faces together with a measured force. An example is an Instron Universal Testing Machine. The test is carried out by placing the cylindrical tablet between the platens (confronting planer faces) of the Testing Machine, so that the platens contact the curved surface of the cylinder at either end of a diameter through the tablet. The sample tablet is then compressed diametrically, suitably by advancing the platens of the machine towards each other at a slow rate such as 1cm/min until fracture of the tablet occurs at which point the applied load required to cause fracture is recorded. The diametral fracture stress is then calculated from the following equation:

$$\delta_O = \frac{2P}{\pi \; Dt}$$

where $\delta_O$ is the diametral fracture stress in Pascal (Pa), P is the applied load in Newtons (N) to cause fracture, D is the tablet diameter in metres (M) and t is the tablet thickness also in metres(M).

For any given tablet composition, tablet strength varies inversely to the air volume expressed as percentage of the whole volume. If tablets have a shape which is not cylindrical, their diametral fracture stress is defined as the diametral fracture stress of cylindrical tablets having the same composition and percentage air volume and hence the same density.

The present invention proves particularly useful when compacting tablets with sufficient pressure to achieve a diametral fracture stress or equivalent parameter of at least 8KPa, better at least 10KPa, and preferably not more than 60KPa. A value not exceeding 25 or 30KPa will often be adequate, but higher values in a range from 20 or 25 KPa up to 60 KPa may be used.

In a second aspect this invention provides a process for the manufacture of tablets of detergent composition, comprising compacting a particulate composition in a mould consisting of a plurality of mould parts which are movable relative to each other, wherein at least one of the mould parts has an elastomeric coating on a surface area which contacts the composition, which elastomeric layer has a thickness of more than 0.5mm, and wherein compaction is carried out with sufficient pressure to form tablets with a DFS in the range 8 to 60KPa.

The amount of compaction pressure needed to attain a desired value of diametral facture stress can be found by making tablets of the chosen composition using varying amounts of applied force, and then measuring the strength of the resulting tablets.

As mentioned above, the tableting press may conveniently have one or two movable dies which are driven into a cavity. The elastomeric layer is, suitably, applied to the faces of the movable dies which apply pressure to the composition, and/or to a stationary counter member towards which a die is driven.

It is conceivable, but not preferred, that the elastomeric layer could be provided on only one die of a pair, or on a stationary counter member facing a single die, yet not on the die. Such arrangements would be expected to lead to asymmetric tablets in which one face was more permeable than the opposite face. This would still give the benefit of enhanced water penetration into the tablet, albeit through one, not both, faces.

An example of a tableting press used in accordance with the invention will now be described, with reference to Figs. 1 to 4 of the accompanying drawings in which:-

Fig. 1 is a vertical cross-section through a tablet press illustrating its general arrangement; and

Figs. 2, 3 and 4 are similar cross-sections showing stages in the cycle of operations of the tablet press.

The invention can be put into effect using a conventional stamping press. A suitable press will generally have a pair of mould parts which move relatively towards and away from each other to compact particulate material between them. They may move within a surrounding sleeve or similar structure.

A suitable arrangement, as illustrated in GB-A-2276345 is shown in Figs. 1 to 4 of the accompanying drawings. The apparatus is a tabletting press, whose structure incorporates a tubular sleeve 10 into which fit a lower punch 12 and an upper punch 14. The sleeve 10 defines a mould cavity 16 closed at its bottom by the lower punch 12. In use a particulate composition is supplied to this cavity by means of a filling shoe 18 which slides on the upper surface 20.

Initially the filling shoe advances to the position shown in Fig. 2 with the upper punch 14 raised. A particulate composition falls from the filling shoe to fill the cavity 16 above the lower punch 12.

Next as seen in Fig. 3 the filling shoe withdraws and the upper punch 14 is pressed down into the cavity 16 thus compacting the particulate composition in the cavity to form a shaped article such as a tablet. Next, as shown in Fig. 4, the upper punch 14 is raised and the lower punch 12 is also raised until the tablet 22 lies at a level with the surface 20. After this the filling shoe 18 advances, pushing the tablet 22 away as it does so while the lower punch descends to the position shown in Fig. 2 for the cycle of operations to be repeated.

In accordance with this invention, the upper punch 12 and the lower punch 14 each have an elastomeric layer over their faces which come into contact with the detergent composition.

The sleeve 10, which also forms part of the mould, is made of steel and is not surfaced with elastomer. The punches 12,14 and also tablets compacted in the mould make sliding contact with this sleeve.

Elastomers are polymers which are deformable, but return to approximately their initial dimensions and shape upon release of the deforming force. Generally they are polymers with long flexible chains, with some cross-linking between chains so as to form a cross-linked network structure. The network structure restrains the movement of the macro-molecular chain molecules and as a result recovers rapidly after deformation.

The term "elastomeric" as used in defining this invention includes materials as defined in ISO (International Standard Organisation) 1982 as an "elastomer", or "rubber". Also included in the definition of "elastomeric" materials according to the invention are thermoplastic elastomers and copolymers and blends of elastomers, thermoplastic elastomers and rubbers.

At low temperature, elastomers are hard and brittle. Then with increasing temperature an elastomer goes through a rubbery phase after softening and retains its elasticity and elastic modulus until its decomposition temperature is reached. The material should of course be in its rubbery state at the operating temperature of the press.

Preferably the elastomeric material according to the invention is selected from those classes described in American Society for Testing and Materials D1418 which include:-

1. Unsaturated carbon chain elastomers (R Class) including natural rubbers and butadiene acrylonitrile copolymer, e.g. "Perbunan" ex Bayer.

2. Saturated carbon chain elastomers (M Class) including ethylene-propylene types, e.g. "Nordel" ex DuPont and fluorine containing types, e.g. "Viton" ex DuPont.

3. Substituted silicone elastomers (Q Class), e.g. as available from Dow Corning.

4. Elastomers containing carbon, nitrogen and oxygen in the polymer chain (U Class), e.g. polyurethane ex Belzona.

Additional materials, for example fillers, can be incorporated in the elastomeric material to modify its mechanical and processing properties. The effects of filler addition depends on the mechanical and chemical interaction between the elastomeric material and the filler.

Fillers can be used to improve tear resistance for example. Suitable fillers include carbon blacks; silicas; silicates; and organic fillers such a styrene or phenolic resins. Other optional additives include friction modifiers and antioxidants.

Materials suitable for the elastomeric layer in the present invention will preferably have a modulus of elasticity, in the range 0.1 to 50MPa, most preferably 1 to 35MPa. The layer thickness is preferably at least 0.7mm, and will often lie in the range 0.7 to about 2.0mm, although thicker layers can be employed, eg up to about 3mm thickness.

The elastomeric layer may be a piece, such as a disc, cut from a sheet of elastomer and secured to the die surface with adhesive. Some elastomers can be applied as a coating on the die, but this is not preferred as a route for producing layers more than 0.5mm thick.

Mould parts, to which an elastomeric layer is applied in accordance with this invention, will generally be metallic, most usually steel. Other rigid materials such as ceramics may possibly be used.

A mould surface may be subjected to pre-treatment to improve the bond strength between the surface and the elastomeric layer. The aim of pre-treatment is to remove weak boundary layers, for example weak oxides on metals; optimise the degree of contact between surface and coating and/or alter the surface topography such that the bondable surface area is increased, and to protect the surface before bonding to it.

Notably a surface may be treated by mechanical abrasion - techniques include wire brushing abrasion papers, and blasting techniques such as water, grit, sand or glass bead blasting.

The application of elastomer layers to dies will generally involve removing the dies from the press, and it may be convenient to maintain a stock of dies in readiness for use - which is reasonably practicable for industrial production.

Adhesives suitable for securing an elastomer layer to a rigid mould surface include two-part epoxy resin and one-part cyanoacrylate types. Two-part epoxy resin adhesive is sold under the trade mark "Araldite" by Ciba-Geigy Plastics, Duxford, England.

The particulate composition which is compacted may be a mixture of particles of individual ingredients, or may comprise particles which themselves contain a mixture of ingredients. Such particles containing a mixture of ingredients may be produced by a granulation process and may be used alone or together with particles or single ingredients.

A detergent composition which is to be made into tablets will normally contain detergent active and detergent builder. Other ingredients are optional, but usually there will be some other ingredients in addition to the detergent active and detergency builder.

The amount of detergent active in a bar or tablet is suitably from 2 to 60wt% and is preferably from 5 or 8wt% up to 40 to 50wt%. Detergent-active material present may be anionic (soap or non-soap), cationic, zwitterionic, amphoteric, nonionic or any combination of these.

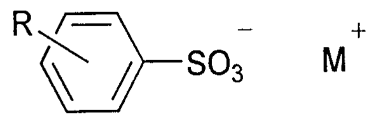
Anionic detergent-active compounds may be present in an amount of from 0.5 to 40 wt%, preferably from 2 or 4% to 30 or 40 wt%, yet more preferably from 8 to 30 wt%.

Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Primary alkyl sulphate having the formula

$$ROSO_3^- \ M^+$$

in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms especially 10 to 14 carbon atoms and $M^+$ is a solubilising cation especially sodium, is commercially significant as an anionic detergent active. Linear alkyl benzene sulphonate of the formula



where R is linear alkyl of 8 to 15 carbon atoms and $M^+$ is a solubilising cation, especially sodium, is also a commercially significant anionic detergent active.

Frequently, such linear alkyl benzene sulphonate or primary alkyl sulphate of the formula above, or a mixture thereof will be the desired anionic detergent and may provide 75 to 100wt% of any anionic non-soap detergent in the composition.

In some forms of this invention, the amount of non-soap anionic detergent lies in a range from 0.5 to 15 wt% of the composition.

It may also be desirable to include one of more soaps of from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rapeseed oil.

Suitable nonionic detergent compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide.

Specific nonionic detergent compounds are alkyl ($C_{8-22}$) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic $C_{8-20}$ primary or secondary alcohols with ethylene oxide, copolymers of ethylene oxide and propylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine. Other so-called nonionic detergent compounds include long-chain amine oxides, tertiary phosphine oxides, and dialkyl sulphoxides.

Especially preferred are the primary and secondary alcohol ethoxylates, especially the $C_{10-15}$ primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

In certain forms of this invention the amount of nonionic detergent lies in a range from 2 to 40%, better 3, 4 or 5%

to 30% by weight of the composition, yet more preferably from 3, 4 or 5% up to 10 or 15% by weight of the composition.

Since the nonionic detergent compounds are generally liquids, these may be absorbed on a porous carrier. Preferred carriers include zeolite, sodium perborate monohydrate and Burkeite (spray-dried sodium carbonate and sodium sulphate as disclosed in EP 221776 (Unilever).

Products of this invention also include detergency builder and this may be provided by water-soluble salts or by water-insoluble material.

Examples of water-soluble builders are sodium tripolyphosphate, pyrophosphate and orthophosphate; soluble carbonates, e.g. sodium carbonate; and organic builders containing up to six carbon atoms, e.g. sodium tartrate, sodium citrate, trisodium carboxymethyloxysuccinate.

In particular phosphate or polyphosphate detergency builder may provide at least 5% by weight, often at least 10% by weight of the overall composition.

Alkali metal (preferably sodium) aluminosilicates are water-insoluble builders. They may be incorporated in amounts of up to 60% by weight (anhydrous basis) of the composition, and may be either crystalline or amorphous of composition, and may be either crystalline or amorphous of mixtures thereof, having the general formula:

$$0.8 - 1.5\ Na_2O.Al_2O_3.\ 0.8 - 6\ SiO_2$$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 $SiO_2$ units (in the formula above).

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well known commercially available zeolites A and X, and mixtures thereof. Also of interest is the novel zeolite P described and claimed in EP 348070 (Unilever). Zeolite P of this type is supplied by Crosfields, Warrington, UK under the designation "Zeolite A24".

Another category of water-insoluble material which can function as a water-softening agent and detergency builder is the layered sodium silicate builders disclosed in US-A-4464839 and US-A-4820439 and also referred to in EP-A-551375.

These materials are defined in US-A-4820439 as being crystalline layered sodium silicate of the general formula

$$NaMS_i0_{2x+1} \quad . \quad YH_2O$$

where M denotes sodium or hydrogen,
x is from 1.9 to 4 and y is from 0 to 20.

Other builders may also be included in the detergent composition as necessary or desired. Water-soluble builders may be organic or inorganic. Inorganic builders that may be present include alkali metal (generally sodium) carbonate; while organic builders include polycarboxylate polymers, such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates, monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono- di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates; and organic precipitant builders such as alkyl- and alkenylmalonates and succinates, and sulphonated fatty acid salts.

Especially preferred supplementary builders are polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%; and monomeric polycarboxylates, more especially citric acid and its salts.

The total amount of detergency builder will generally lie in a range from 5 to 80wt% of the composition. The amount may be at least 10 or 15wt% and may lie in a range up to 50 or 60wt%.

Tablets for addition to a washing machine preferably include a binder material which is water-soluble and also serves as a disintegrant by disrupting the structure of the tablet when the tablet is immersed in water, as taught in our EP-A-522766.

Preferred is that at least some of the particles of the detergent composition are individually coated with the binder material. Then, when the composition is compacted, this coating serves as a binder distributed within the composition.

Use of a binder helps to hold the tablet together, thus enabling it to be made using a lower compaction pressure and making it inherently more likely to disintegrate well in the wash liquor. If the binder is also a material that causes disruption when contacted with water, even better disintegration properties may be achieved.

It is preferred that the binder material should melt at a temperature of at least 35°C, better 40°C or above, which is above ambient temperatures in many temperate countries. For use in hotter countries it will be preferable that the melting temperature is somewhat above 40°C, so as to be above the ambient temperature.

For convenience the melting temperature of the binder material should be below 80°C.

Preferred binder materials are synthetic organic polymers of appropriate melting temperature, especially polyethylene glycol. Polyethylene glycol of average molecular weight 1500 (PEG 1500) melts at 45°C and has proved suitable. Polyethylene glycol of higher molecular weight, notably 4000 or 6000, can also be used.

Other possibilities are polyvinylpyrrolidone, and polyacrylates and water-soluble acrylate copolymers.

The binder may suitably be applied to the particles by spraying, e.g. as a solution or dispersion. The binder is preferably used in an amount within the range from 0.1 to 10% by weight of the tablet composition, more preferably the amount is at least 1% or even at least 3% by weight of the tablets. Preferably the amount is not over 8% or even 6% by weight.

Detergent compositions which are compacted into shaped articles according to the invention may contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching action at low wash temperatures. If any peroxygen compound is present, the amount is likely to lie in a range from 1 to 30% by weight of the composition.

Perphthalimido perhexanoic acid and perdodecanoic acid are two examples of organic peroxyacids. Typically these can be used as 1 to 6% of the composition.

Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylethylene diamine (TAED), now in widespread commercial use in conjunction with sodium perborate; and perbenzoic acid precursors. Typically persalt is used as 5 to 30% by weight of a composition, while activator is 1 to 10% by weight of the composition.

Other ingredients may also be present in the overall composition. These include sodium carboxymethyl cellulose, colouring materials, enzymes, fluorescent brighteners, germicides, perfumes and bleaches. Sodium alkaline silicate may be included, although the amount of this or at least the amount added as an aqueous liquid, is preferably restricted so as to keep to a particulate mixture prior to compaction.

The starting particulate composition which is compacted in accordance with this invention may in principle have any bulk density. However, we have preferred to utilise powders of relatively high bulk density. Thus the starting particulate composition may suitably have a bulk density of at least 500 g/litre, preferably at least 600 g/litre, and advantageously at least 700 g/litre.

Granular detergent compositions of high bulk density prepared by granulation and densification in a high-speed mixer/granulator, as described and claimed in EP 340013A (Unilever), EP 352135A (Unilever), and EP 425277A (Unilever), or by the continuous granulation/densification processes described and claimed in EP 367339A (Unilever) and EP 390251A (Unilever), are inherently suitable for use in the present invention.

Most preferred are granular detergent compositions prepared by granulation and densification in the high-speed mixer/granulator (Fukae mixer), as described in the above-mentioned EP 340013A (Unilever) and EP 425277A (Unilever).

EXAMPLE 1

A detergent powder with the following composition was prepared:

| Granulated Components | % by weight |
|---|---|
| coconut primary alkyl sulphate | 1.4 |
| coconut alcohol 3EO | 7.6 |
| coconut alcohol 6EO | 4.8 |
| zeolite A24 | 29.3 |
| soap | 2.9 |
| sodium carboxymethyl cellulase | 0.8 |
| sodium carbonate | 0.3 |
| water | 5.3 |
| Postdosed Components | |
| PEG 1500 | 4.3 |
| sodium percarbonate (borosilicate coated) | 19.5 |
| TAED granule | 4.2 |
| perfume | 0.6 |
| antifoam, fluorescer and heavy metal sequestrant | 4.0 |
| sodium citrate | 15.0 |

The materials listed as "granulated components" were mixed in a Fukae (Trade Mark) FS-100 high speed mixer-granulator. (Continuous granulation equipment could also be used, as could other machinery for granulating in batches.) The soap was prepared in situ by neutralisation of fatty acid with sodium hydroxide. The mixture was granulated and densified to give a powder of bulk density greater than 750 g/litre and a mean particle size of approximately 650$\mu$m.

The powder was sieved to remove fine particles smaller than 180$\mu$m and large particles exceeding 1700$\mu$m. The remaining solids were then mixed with the powder in a rotary mixer, after which the perfume was sprayed on, followed by the PEG. The PEG was sprayed at about 80°C onto the powder which was at about 22-26°C (slightly above ambient because of frictional heating during granulation).

Detergent tablets were prepared by compaction of 50g quantities of the detergent powder formulation using apparatus as illustrated in Figs. 1 to 4. The tablets were of circular cross-section having a diameter of 4.5 cm and a thickness of approximately 2.5 to 3.1 cm.

Compaction of the detergent powder, to make tablets, was carried out using either plain steel top and bottom punches, or alternatively punches which had an elastomer layer on their faces which contact the detergent composition.

More specifically, one set of punches was given a polyurethane coating painted on as a solvent solution and providing a thickness of approximately 250μm after evaporation of solvent. Another set of punches was provided with an elastomer layer in accordance with the present invention, 1mm thick and glued on to the steel punches.

With each set of punches 100 tablets were produced after which the top punch was inspected.

With steel punches, the top punch was found to have 0.3 to 0.6g of powder firmly adhering to it, and producing indentations in the tablet surfaces.

With both sets of punches bearing an elastomeric layer, the top punch was found to have only about 0.01g of powder adhering to it. This was a light dusting which was easily removed. If a larger quantity of tablets was to be made, it would be possible to run the press for an extended period without needing frequent stops to clean the punches.

In a comparative experiment, a similar detergent composition was compacted in the same way, but with a self-adhesive polytetrafluoroethylene coating on the upper and lower punches. After producing batches of 100 tablets it was found that 0.1 to 0.6 g of detergent powder had become firmly adhered to the punch surfaces.

The flat surfaces of tablets made with these punches were inspected visually. It was apparent that when tablets were made with steel punches the first tablets produced had smooth faces. After running the press for some time the tablets had rougher surfaces but the roughness was attributable entirely to material which had become adhered to the dies. By contrast when tablets were made using dies surfaced with elastomer 1mm thick the surfaces were rougher than the surfaces of either of the first tablets made with steel dies and tablets made with dies having a thin elastomer coating. In the case of tablets made using dies with the thick elastomer coating in accordance with the present invention the individual particles of the composition could still be discerned at the surface of the tablets.

This result which was apparent from inspection by eye was also confirmed by laser profilometry.

The strength of tablets made with these various dies was tested by the test of diametral fracture stress described earlier.

<u>Capillary uptake test</u>

The speed at which the tablets took up water on immersion was tested by a procedure in which the weight of a tablet is checked and then the tablet is placed with one of its flat faces resting on a horizonal gauze support in a dish.

Water, coloured with ink, is poured into the dish until the level of water contacts the lower face of the tablet resting on the gauze. After 1 minute the tablet is removed, any superficial water is shaken off and the tablet is weighed. The increase in weight of the tablet is an indication of the rate at which water is taken up through capillary action. The results obtained were:

| | DFS | Capilliary uptake (gm) |
|---|---|---|
| Thick elastomer (1mm) | 12.4 | 4.2 |
| Thin elastomer (250$\mu$m) | 12.5 | 3.2 |
| No elastomer | 10.3 | 3.4 |

<u>Water uptake (partially submerged)</u>

In another test the procedure is similar except that the water coloured with ink is poured into the dish until it is nearly at the same level as the top surface of the tablet, although this top surface is not itself covered by water.

After a period of time, which in this Example was 30 seconds, the tablet is removed from the dish and the gain in weight is measured. As the water and ink penetrate into the tablet the tablet takes on the dark colour of the ink. It is observed whether the dark colour of the ink is visible over the whole of the top face of the tablet (which was not wetted directly) or whether a disc of light colour can still be seen on this top face of the tablet. If such a disc can be seen its diameter is measured. The results of these tests are set out in the following table.

| | DFS | Water uptake (gm) | Diameter of dry core (mm) |
|---|---|---|---|
| Thick elastomer (1mm) | 12.4 | 9.3 | 11.2 |
| Thin elastomer (250μm) | 12.5 | 7.8 | 20.3 |
| No elastomer | 10.3 | 8.1 | 17.9 |

Uptake of water by the tablets made using the dies surfaced with thick elastomer was calculated to be approximately the whole of the available porosity (void space) in the tablets. The porosity was calculated to be approximately 25% by volume.

EXAMPLE 2

Detergent powder of the following composition was prepared by the same procedure as in Example 1:

| Granulated Components | % by weight |
|---|---|
| coconut primary alkyl sulphate | 1.4 |
| coconut alcohol 5EO | 11.7 |
| zeolite A24 | 27.7 |
| soap | 2.7 |
| sodium carboxymethyl cellulase | 0.8 |
| sodium carbonate | 0.3 |
| water | 8.8 |
| **Postdosed Components** | |
| PEG 1500 | 4.0 |
| sodium perborate tetrahydrate | 18.5 |
| TAED granule | 4.0 |
| perfume | 0.4 |
| antifoam, fluorescer and heavy metal sequestrant | 4.0 |
| sodium citrate | 14.2 |
| sodium polyacrylate | 1.6 |

The detergent composition was sieved to remove particles smaller than 200$\mu$m and stamped into tablets using plain steel dies and (separately) using dies surfaced with elastomer. Various levels of compaction force were employed with each set of dies.

Elastomer A was 1mm thick and had elastic modulus of 0.72MPa. Elastomer B was 1mm thick and had elastic modulus 9.83MPa.

The tablets were tested to determine their density, porosity, strength and water uptake. The results are tabulated below. The test of water uptake was the test in which the tablet was partially submerged, leaving its upper face exposed to air, as described in the previous example, but with varying periods of time, as indicated.

| DIE COATING | TABLET DENSITY (gm/litre) | DFS (kPa) | WATER UPTAKE (gm) | PERIOD OF PARTIAL IMMERSION (seconds) | OBSERVATIONS |
|---|---|---|---|---|---|
| No Elastomer | 1190 | 22.7 | 5.1 | 60 | core left |
| No Elastomer | 1130 | 12.8 | 6.8 | 60 | core left |
| No Elastomer | 1096 | 9.2 | 8.3 | 60 | |
| No Elastomer | 1040 | 4.5 | 9.9 | 30 | |
| No Elastomer | 1040 | 4.5 | collapsed | 60 | |
| Elastomer A | 1190 | 21.9 | 5.7 | 60 | dry core left |
| Elastomer A | 1130 | 13.1 | 8.1 | 60 | small core left |
| Elastomer A | 1090 | 9.1 | collapsed | 40 | |
| Elastomer A | 1090 | 9.1 | 8.9 | 30 | |
| Elastomer A | 1040 | 4.6 | collapsed | 30-40 | |
| Elastomer A | 1040 | 4.6 | 9.4 | 15 | |
| Elastomer B | 1080 | 20.8 | 5.5 | 60 | dry core left |
| Elastomer B | 1130 | 13.9 | 8.2 | 60 | |
| Elastomer B | 1090 | 8.9 | 9.9 | 30 | |
| Elastomer B | 1090 | 8.9 | collapsed | 50 | |
| Elastomer B | 1040 | 4.9 | 10.7 | 15 | |
| Elastomer B | 1040 | 4.9 | collapsed | 30 | |

By comparing results at similar porosity and strength, it can be seen that tablets with similar density, porosity and strength had greater water uptake when made with elastomer-faced dies.

EXAMPLE 3

Tablets for use in fabric washing were made, starting with a spray-dried base powder of the following composition:

| Ingredient | PARTS BY WEIGHT |
|---|---|
| Sodium linear alkylbenzene sulphonate | 11.0 |
| $C_{13-15}$ fatty alcohol 7EO | 2.4 |
| $C_{13-15}$ fatty alcohol 3EO | 2.3 |
| Sodium tripolyphosphate* | 18.0 |
| Sodium silicate | 4.0 |
| Soap | 0.21 |
| Acrylate/maleate copolymer | 1.5 |
| Sodium sulphate, moisture and minor ingredients | balance to 45 |

* Added to the slurry as anhydrous sodium tripolyphosphate containing at least 70% phase II form.

This powder was then mixed with other ingredients as tabulated below. These included particles of sodium tripolyphosphate specified to contain 70% phase I form and contain 3.5% water of hydration (Rhodia-Phos HPA 3.5 available from Rhone-Poulenc).

| Ingredient | % by weight |
|---|---|
| Base powder | 45 |
| Sodium percarbonate granules | 15 |
| TAED granules | 3.4 |
| Anti-foam granules | 3.2 |
| Perfume, enzymes and other minor ingredients | 3.5 |
| Rhodiaphos HPA3.5 tripolyphosphate | 30 |
| Sodium carbonate | - |

40g portions of this particulate composition were made into cylindrical tablets of 44 mm diameter, using a press fitted with punches elastomer surface layers about 2mm thick.

The press was set to apply compaction force of approximately 10KN corresponding to a pressure of about 6 or 7 MPa which was sufficient to produce tablets with a diametral fracture stress of about 25 KPa.

CLAIMS:

1. Use of an elastomeric layer, more than 0.5mm thick, on a surface area of at least one mould part in a press for compacting particulate detergent composition into tablet form, which surface area contacts the composition during compaction;

in order to enhance the penetration of water through the tablet surface on immersion.

2. Use according to claim 1, wherein the particulate detergent composition has a bulk density, prior to compaction, of at least 650g/litre.

3. Use according to claim 1 or claim 2, wherein the compacted tablets contain between 20 and 35% air by volume.

4. Use according to any one of claims 1 to 3, wherein the compacted tablets have a diametral fracture stress as defined herein in the range 8 to 60KPa.

5. A process for the manufacture of tablets of detergent composition, comprising compacting a particulate composition in a mould consisting of a plurality of mould parts which are movable relative to each other, characterised in that at least one of the mould parts has an elastomeric coating on a surface area which contacts the

composition, which elastomeric layer has a thickness of more than 0.5mm and that compaction is carried out with sufficient pressure to form tablets with a diametral fracture stress (DFS) as herein defined in the range 8 to 60KPa.

6. Process according to claim 5, wherein the particulate detergent composition has a bulk density, prior to compaction, of at least 650g/litre.

7. Process according to claim 5 or claim 6, wherein the compacted tablets contain between 20 and 35% air by volume.

8. A process according to any one of claims 4 to 7 wherein said elastomer layer has a thickness in a range from 0.7 to 2.0mm.

9. A process according to any one of claims 4 to 8 wherein the tablets have a diametral fracture stress of 10 to 30 KPa.

10. A process according to any one of claims 4 to 9 wherein the composition contains from 5 to 40% by weight of detergent and from 10 to 60% by weight of detergency builder, optionally together with other ingredients.

Fig.1.

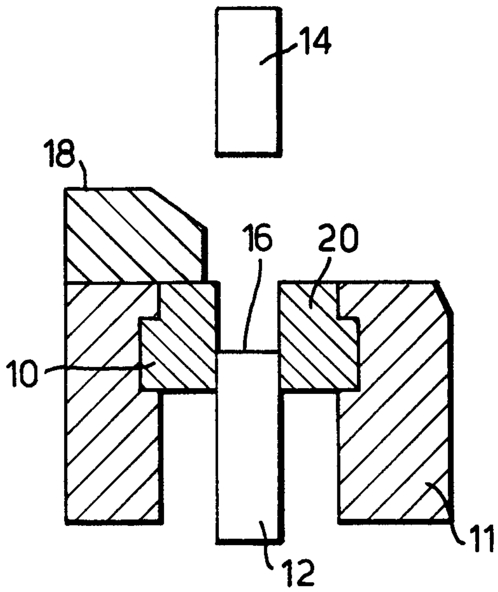



Fig.2.

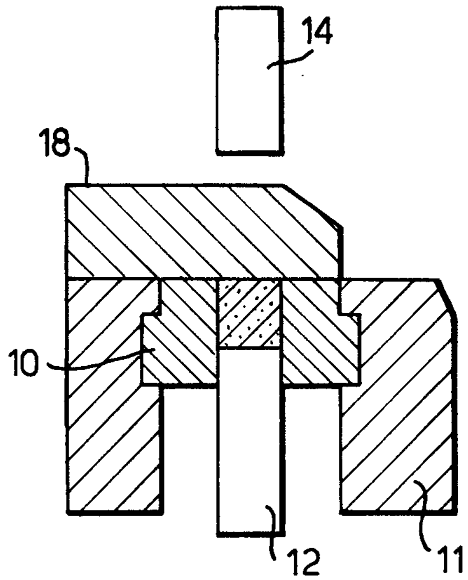



Fig.3.

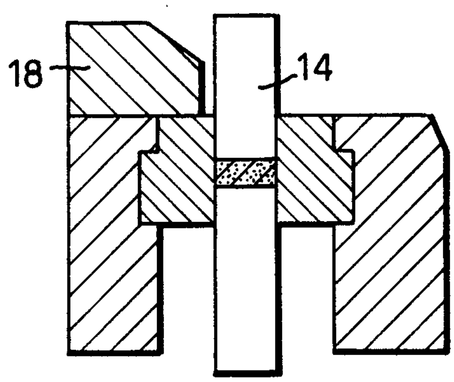
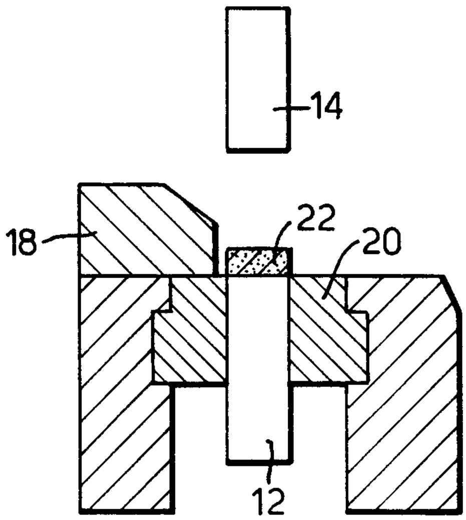



Fig.4.



# INTERNATIONAL SEARCH REPORT

Internatio .pplication No
PCT/EP 98/02189

A. CLASSIFICATION OF SUBJECT MATTER

C 11 D 17/00

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 11 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | GB 2276345 A (UNILEVER PLC) 28 September 1994 (28.09.94), the whole document (cited in the application). -- | 1-10 |
| A | WO 97/20028 A1 (UNILEVER PLC) 05 June 1997 (05.06.97), claims (cited in the application). -- | 1-10 |
| A | GB 2260989 A (UNILEVER PLC) 05 May 1993 (05.05.93), claims (cited in the application). ---- | 1-10 |

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 13 August 1998 | 11.09.98 |

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