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**(54) PROCESS FOR THE MANUFACTURE OF SHAPED ARTICLES FROM DETERGENT
COMPOSITIONS**

VERFAHREN ZUR HERSTELLUNG VON FORMKÖRPERN AUS
REINIGUNGSMITTELNZUSAMMENSETZUNGEN

PROCEDE DE FABRICATION D'ARTICLES FACONNES A PARTIR DE COMPOSITIONS
DETERGENTES

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DescriptionTECHNICAL FIELD

5 [0001] The present invention relates to the manufacture of detergent compositions in the form of shaped articles of compacted detergent powder.

BACKGROUND AND PRIOR ART

10 [0002] One known category of detergent product in the form of a shaped solid article is a non-soap detergent bar used for the handwashing of fabrics and sometimes also used for cleaning fixed surfaces. Such bars are used by rubbing on the fabric or surface. A layer of the bar wears away (e.g. is transferred to the fabric or the wash liquor) but after use the remainder of the bar can be set aside and stored for use on a future occasion.

15 [0003] GB-A-2260989 discloses that such reusable bars can be manufactured by stamping a particulate composition to compact it into shaped solid form. This is done using a high compaction pressure so as to obtain a bar of low porosity which retains its integrity when in contact with water. Typically the air within such bars will be less than 15% of bar volume. Such bars generally are made with a size weighing 100g or more.

20 [0004] Another known category of detergent product in the form of a shaped solid article is a non-soap detergent tablet which is added to a washing machine at the start of the wash as an alternative to using a powdered or a liquid detergent composition. Such tablets are formulated for a solutionwashing process with the intention that the soluble components of the tablet will dissolve rapidly and that the tablet will break up completely in the wash water giving a wash liquor whose composition is similar to that which would be given by the use of a detergent powder or liquid.

25 [0005] 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.

30 [0006] Detergent tablets are described, for example, in GB-A-911204 (Unilever), US-A-3953350 (Kao), EP-A-522766 (Unilever); and have been sold commercially in Spain.

[0007] Detergent tablets are generally made by compressing or compacting a detergent powder, which includes non-soap detergent active and detergency builder. Tablets typically weigh 10 to 160g more especially 10 or 15 up to 100g, and have a porosity such as to contain 15% or more of air, by volume.

35 [0008] Processes are also known for stamping toilet soap bars, for example as described in GB-A-746,769. However, such toilet bars are typically stamped from solid billets. There are significant differences between the handling and processing of such billets and powdered detergent compositions.

[0009] For example, it is desirable that the stamped articles have smooth surfaces. Extruded toilet soap bars have smooth surfaces as a result of the extrusion process. However, a smooth finish cannot be guaranteed in compacted detergent powder bars.

40 [0010] Compaction of detergent powder to make shaped solid articles has been carried out using a press with steel dies or punches which contact the powder and compact it into the shaped article.

[0011] 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.

45 [0012] GB-A-2276345 proposes an alternative approach, which is to use mould parts bearing an elastomeric coating. Thus this document discloses a process for the manufacture of articles, including tablets and bars of compacted detergent powder, using mould parts surfaced with an elastomeric material of some thickness. 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.

50 [0013] The application of these thick coatings is apt to be complex and may require equipment which cannot easily be provided at the place where the mould parts are used.

[0014] Surprisingly, we have now found that good release of shaped articles such as tablets and bars from mould parts can be achieved with thinner coatings. This has practical advantages, because thin coatings are easier to apply to mould parts and recoating may be carried out at the manufacturing facility where the mould parts are used.

55 [0015] We have found that thin elastomer films on punch surfaces lead to bars with smooth surfaces whereas thicker elastomer coatings produce rougher surfaces. A smooth surface is valuable because of consumer fears that a rough surface will damage fabrics when used.

[0016] Smoothness may be measured by the procedure described in relation to the examples below.

[0017] Thus, for bars which are to be used for handwashing, a thin elastomer coating on mould parts has the advantage of low adhesion to the shaped article, combined with the advantage of a smooth surface. Neither steel nor a

thick elastomer coating provides both of these advantages in combination.

[0018] Therefore, the present invention provides a process for the manufacture of shaped solid articles by compacting a particulate detergent composition in a mould having a plurality of mould parts which are movable relative to each other, at least one of the mould parts having an elastomeric coating on a surface area which contacts the composition characterised in that the elastomeric coating has, over a majority, i.e. more than half of its area, a thickness of at least 5 micrometers and not exceeding 490 micrometers.

[0019] Preferably the coating does not exceed this thickness over 90% or more of its area.

[0020] Such coatings are preferably applied as a liquid - either a solution or a melt, and allowed to solidify by evaporation of solvent, cross-linking or cooling, as appropriate.

[0021] In a further aspect this invention provides a process for the manufacture of shaped solid articles by compacting a particulate detergent composition in a mould having a plurality of mould parts which are movable relative to each other, at least one of the mould parts having an elastomeric coating on a surface area which contacts the composition characterised by applying the coating as a liquid to at least one mould part and allowing or causing it to solidify on the mould part, at least part of the coating having a thickness as described above.

[0022] Preferably, the present invention comprises the step of delivering particulate detergent to a cavity, the cavity being at least partially defined by at least one of the mould parts. Preferably, the cavity is defined by a sleeve and at least one mould part, the said at least one mould part being preferably movable within the sleeve. Preferably, the other mould part is also movable into this sleeve.

[0023] Means such as air extraction channels may be provided as is known to the skilled person, to allow removal of air during compaction.

[0024] In many instances the invention will include periodically renewing the coating.

LIST OF DRAWINGS

[0025] This application includes the following drawings:-

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

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

Fig. 5 is a diagrammatic view, partly in vertical cross-section, of experimental apparatus; and

Fig. 6 is a graph of force against time obtained with the apparatus of Fig. 5.

DETAILED DESCRIPTION AND EMBODIMENTS

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] In accordance with this invention, the upper punch 12 and the lower punch 14 each have a thin elastomeric coating over their faces which come into contact with the detergent composition.

[0031] The sleeve 10, which also forms part of the mould, is made of steel and is not coated with elastomer. The punches 12,14 and also tablets compacted in the mould make sliding contact with this sleeve.

[0032] 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 compaction step can be adjusted to produce shaped solids with a range of porosities. For detergent bars to be used in handwashing, then put aside and later reused, a porosity of not over 15% air by volume, better not greater than 12% is desirable. A high pressure can reduce porosity to as low as 1% air by volume. So, the preferred porosity is 1 to 15% more preferably 3 to 10% air by volume.

[0033] The force applied to the powdered detergent depends upon the final porosity desired. For example, the force may be in the region 50-100 kN.

[0034] The air content of a shaped solid product can be calculated from the volume and weight of the product, provided the airfree 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.

[0035] Detergent tablets intended to break-up and dissolve/dispose in water are generally compacted with less applied pressure so as to be more porous. A porosity of more than 15 or 20% by volume is typical.

ELASTOMERS AND THEIR APPLICATION TO MOULD PARTS

[0036] 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.

[0037] 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.

[0038] 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.

[0039] Thermoplastic elastomers consist of amorphous and crystalline phases. The amorphous phase has a softening range below ambient temperature and thus acts as an elastic spring whilst the crystalline segments whose softening range is above ambient temperature, act as cross-linking sites.

[0040] Preferably the elastomeric material according to the invention is selected from those classes described in American Society for Testing and Materials D1418 which include:-

- 25 1. Unsaturated carbon chain elastomers (R Class) including natural rubbers. E.g. Standard Malaysian Rubber; butadiene acrylonitrile copolymer, e.g. "Perbunan" ex Bayer.
- 30 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.
- 35 3. Substituted silicone elastomers (Q Class) including liquid silicone rubbers, e.g. Silastic 9050/50 P (A+B) ex Dow Corning.
- 40 4. Elastomers containing carbon, nitrogen and oxygen in the polymer chain (U Class) including polyurethane, e.g. polyurethane ex Belzona.

[0041] Suitable elastomeric coatings can be obtained from materials such as liquid silicone rubbers such as Silastic 9050/50 P A+B (ex Dow Corning) which after curing has a modulus of elasticity about 2-3 MPa; and polyurethane, for example Belzona PU2221, as hereinafter defined, which after curing has a modulus of elasticity of about 9MPa, and Belzona 2131 (MP Fluid Elastomer), a 2 part product based on a diphenylmethane 4,4'-diisocyanate (MDI) system with a phenylmercuric neodecanoate catalyst.

[0042] Additionally materials, for example fillers, can be added to 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.

[0043] Fillers can be used to modify the elastomeric material such that desirable properties, for example tear resistance, is achieved. Suitable fillers include carbon blacks; silicas; silicates; and organic fillers such a styrene or phenolic resins.

[0044] Other optional additives include friction modifiers and antioxidants.

[0045] Materials suitable as elastomeric coatings in the present invention will preferably have a modulus of elasticity, in the range 0.1 to 50MPa, most preferably 1 to 35MPa.

[0046] The modulus of elasticity of an elastomeric coating may be measured by recording the force required to indent the coating as a function of the indentation depth. Typically an indentor with a spherical tip may be employed and the slope, s, of the force as a function of the indentation depth to the power 3/2 is determined. The indentation depth is the movement of an indentor into the coating after it first contacts the surface of the coating. In general, it is necessary to correct the measured indentation depth for the compliance of the measurement apparatus. That is, the actual indentation depth, d, is related to the measured apparent value d' by the following expression

$$d = d' - (F \cdot C)$$

5 where F is the indentation force. The compliance C is determined by compressing the indentor against a rigid surface and recording the apparent displacement as a function of the applied force which has a slope equal to C . The modulus of elasticity E is calculated from the following expression

$$10 E = \frac{3}{4} \cdot s \cdot \frac{1}{\sqrt{R}} \cdot (1 - b^2)$$

where $s = F \cdot d^{3/2}$, R is the radius of the spherical tip of the indentor and b is the Poisson's ratio of the coating which is equal to about 0.5 for elastomers.

[0047] Under certain conditions to be described hereafter, the above indentation method may give falsely large values of the elastic modulus due to the influence of the rigid material onto which the coating is applied. In order to safely avoid this problem it is necessary to ensure that the contact radius of the indentor with the coating does not exceed about 1/10 of the thickness of the coating. The contact radius, a , is related to the indentation depth by the following expression

$$20 a = \sqrt{(dR)}$$

[0048] For coatings less than 200 μm , it is recommended that a nanoindentor is used which is capable of measuring indentation forces at small indentation depths using indentors with tips having a small radius. An example of such equipment is the "NanolIndentor II" (Nano-instruments). For thicker (greater than 200 μm) coatings, more conventional measurement equipment such as an Instron tester, (e.g. Model 5566) may be employed.

[0049] Mould parts, to which elastomeric coatings are applied in accordance with this invention, will generally be metallic, most usually steel. Other rigid materials such as ceramics may possibly be used.

[0050] A mould surface may be subjected to pre-treatment prior to coating with the elastomeric material, to improve the bond strength between the surface and the coating. 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. Suitable techniques can be classified as:-

- 35 1. Mechanical Abrasion - techniques include wire brushing abrasion papers, blasting techniques such as water, grit, sand or glass bead blasting, polishing such as diamond polishing and spark erosion.
2. Chemical Treatment - including solvent cleaning, etching for example using acid, anodising, and use of a primer or adhesive bonding chemical for example a silane or silicone.
- 40 3. Energetic Surface Pre-Treatment such as corona discharge.

[0051] An elastomeric coating can be applied to mould surfaces as a solution in organic solvent. The solvent is allowed to evaporate, leaving a coating of the elastomer on the mould surface.

[0052] The coating solution may be applied by spraying, or by brushing on as if it were paint.

[0053] A thermoplastic elastomeric material may be applied to a mould surface as a melt, and allowed to cool. Once again application may be by brushing or spraying onto the mould surface.

[0054] When an elastomeric material requires cross-linking, this may be in situ on a mould surface by incorporating a cross-linking agent in the coating material before it is applied, but "curing/" the material, so as to bring about the cross-linking, after application to the mould surface.

[0055] When coating becomes worn it can be removed by abrasion, by dissolution or some combination of the two. The mould part can then be recoated, and used again.

[0056] For example silicone coatings can be removed using a solution of potassium hydroxide in a mixture of ethanol and toluene.

[0057] Polyurethane coatings can be removed using organic solvent.

[0058] An elastomeric coating will have a thickness of at least 5, preferably at least 10 micrometres, over a majority, i.e. more than half, of the coating area.

[0059] Preferably the coating will have this minimum thickness over at least 90%, better substantially all, of the coating area.

[0060] Preferably also the coating thickness will not exceed 0.49 mm, i.e. 490 micrometres, over at least 90%, better substantially all, of the coating area.

[0061] The coating thickness may lie in a range up to 400, 450 or even 490 micrometres. Preferred coating thicknesses are in a range up to 300 micrometres.

[0062] Various instruments are available to measure the thickness of surface coatings. Typically a measuring instrument is applied to the coated surface and uses inductive or electromagnetic interaction with the underlying metallic substrate to measure the distance from that substrate and hence the coating thickness. A supplier of such instruments is Elcometer Instruments Ltd., Manchester, England.

10 COMPOSITIONS

[0063] 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.

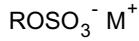
[0064] A detergent composition will normally contain detergent active and detergent builder. Other ingredients are optional, but usually there will be some other ingredients in addition to the detergent active and detergency builder.

[0065] 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.

[0066] 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%.

[0067] Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0068] Primary alkyl sulphate having the formula



30 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, is commercially significant as an anionic detergent active. It is frequently the desired anionic detergent and may provide 75 to 100wt% of any anionic non-soap detergent in the composition.

[0069] 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.

[0070] It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rapeseed oil.

[0071] Suitable nonionic detergent compounds which may be used include in particular the reaction products of 40 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 ether alone or with propylene oxide.

[0072] Specific nonionic detergent compounds are alkyl (C₈-22) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic C₈-20 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.

[0073] Especially preferred are the primary and secondary alcohol ethoxylates, especially the C₁₂-15 primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

[0074] In certain forms of this invention the amount of nonionic detergent lies in a range from 2 to 40%, better 4 or 50 5 to 30% by weight of the composition.

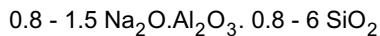
[0075] Since the nonionic detergent compounds are generally liquids, these may be absorbed on a porous carrier. Preferred carriers include zeolite, sodium perborate monohydrate and Burkeite (spray-dried sodium carbonate and sodium sulphate as disclosed in EP 221776 (Unilever)).

[0076] Products of this invention also include detergency builder and this may be provided by water-soluble salts or by water-insoluble material.

[0077] 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.

[0078] In particular phosphate or polyphosphate detergency builder may provide at least 5% by weight, often at least 10% by weight of the overall composition.

[0079] 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 or mixtures thereof, having the general formula:



[0080] 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 SiO₂ units (in the formula above).

[0081] 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, hydroxyethyliminoacetates; and organic precipitant builders such as alkyl- and alkenylmalonates and succinates, and sulphonated fatty acid salts.

[0082] 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.

[0083] 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%.

[0084] A reusable detergent bar which is to be used for handwashing will generally include from 10 to 70wt% of water-insoluble material.

[0085] Such material may be talc, kaolin, calcite or bentonite, as a "filler" which although chemically inert can be significant in contributing to strength and other properties of a detergent bar.

[0086] A reusable bar will generally include from 10 to 70wt% of soluble salts. These may be soluble builders such as tripolyphosphate, and other soluble salts such as sodium silicate or sulphate.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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.

[0091] For convenience the melting temperature of the binder material should be below 80°C.

[0092] 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.

[0093] Other possibilities are polyvinylpyrrolidone, and polyacrylates and water-soluble acrylate copolymers.

[0094] 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.

[0095] 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 10 to 25% by weight of the composition.

[0096] 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.

[0097] 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.

[0098] 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 400 g/litre, preferably at least 500 g/litre, and advantageously at least 700 g/litre.

[0099] 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.

[0100] Most preferred are granular detergent compositions prepared by granulation and densification in the high-speed mixer/granulator (Fukae mixer), as described in the abovementioned EP 340013A (Unilever) and EP 425277A (Unilever).

EXAMPLE 1

[0101] In order to investigate the effect of a range of coatings, detergent bars were made using an experimental apparatus as shown in Fig. 5 of the drawings.

[0102] The mould for the tablets consisted of a steel collar 32 over a bottom plate 34 which was made of steel. A movable punch 36 was driven downwardly into the collar 32 to compress material within the mould and thus form a bar.

[0103] The punch 36 was driven up and down using an Instron (Registered Trademark) Universal testing machine. The ram of this machine is indicated at 38.

[0104] A load cell 40 was interposed between the ram 38 and the movable punch 36. This load cell was connected to data logging equipment 42.

[0105] For each experiment, 250g of a particulate detergent composition was placed inside the collar 32.

[0106] The Instron was then used to drive the punch 36 into the collar 32 at a predetermined rate of movement until it was applying a predetermined load (about 85kN) to the material within the collar. This was sufficient to compact the material into a reusable bar. The punch was then withdrawn by reversing the ram 38 of the Instron.

[0107] Throughout this procedure, the force applied by the ram 38 to the punch 36 was measured by the load cell 40 and recorded by the data logging equipment.

[0108] As the punch is withdrawn, the force exerted on it by the ram 38 becomes negative. The magnitude of this negative force indicates the extent of adhesion between the bar and the surface of the punch.

[0109] A graph of force against time, obtained with a steel punch, is shown at Fig. 6 as an illustration. The maximum (reference number 44, at 4.4 kN in this case) of the negative peak is the magnitude of adhesion.

[0110] Experiments were carried out using the following two particulate detergent compositions.

Formulations	% by weight	
	A	B
Linear alkyl benzene sulphonate	22.0	18.0
Primary alkyl sulphate	-	12.0
Sodium triphosphate	14.0	15.0
Sodium carbonate	2.0	5.4
Sodium sulphate	10.0	9.4
Calcite	16.55	28.4
Kaolin	16.55	-
Microfine silica	5.0	2.0
Sodium sulphate	7.5	-
Calcium hydroxide	1.0	-
Water	3.0	4.3
Minors	2.4	5.5
Total	100.0	100.0

[0111] Each of these compositions was prepared, in the form of a particulate mixture, by granulating the ingredients in a high speed mixer.

[0112] Initially, the granulator was used to mix the solid ingredients, other than the alkylbenzene sulphonate.

[0113] The solids included additional sodium carbonate required for a subsequent neutralisation reaction.

[0114] The agitator speed was reduced, and alkylbenzene sulphuric acid was added over a period of 1 to 2 minutes. A small quantity of water was added, amounting to 2 to 6wt% of the composition. Neutralisation took place and the mixture formed granules. A small quantity of flow aid (finely divided silica) was added which prevented the granules agglomerating together.

[0115] A number of punches were used as the movable upper punch 36. These punches were:

- 10 uncoated steel punch,
- steel punch with coating of polytetrafluoroethylene
- steel punch with relatively thick (2mm) coating of natural rubber
- steel punches with coating of synthetic elastomer 2mm and 8mm thick
- 15 steel punches with thinner silicone rubber coatings.

[0116] To prepare the thin silicone rubber coatings, the punches were first degreased with acetone, and treated with a primer (Dow Corning 3-6060) which comprises 95% methyl isobutyl ketone, 2% ethyl polysilicate, 1% isopropoxybis (acetylacetone) titanium and 2% dimethyl, methylvinyl siloxane, acetoxy-terminated, and was diluted with hexane as required to give a composition suitable for application by brushing.

[0117] The silicone rubber was liquid silicone rubber Silastic 9050-50P Parts A and B, ex Dow Corning. In order to prepare the coating the two parts were mixed at room temperature. The resulting mixture was then brushed onto the punch surface and cured at 200°C.

[0118] Each of these punches was used to make bars of each composition. Adhesion of the punches to the bars was determined from the output of the load cell. The results obtained are set out in the table below.

[0119] The smoothness of the surfaces of the bars was measured. A white silicone rubber was cast on the surface, covering an area about 15mm in diameter, then peeled off after it had cured, so as to provide a white replica surface. A 4mm by 4mm area of the replica surface was scanned with a laser profilometer at 20µm intervals. The accuracy of replica surfaces made in this way was checked by making and scanning more than one replica of the same surface area.

[0120] The profilometer was used to scan the 4mm by 4mm area as 201 lines, each containing 201 points. At each point the instrument determined the height of a spot 1.5µm in diameter, with a resolution of about 0.1µm. For each line scanned, a centre line was established by linear regression, so that a cross-section on the line of scan would have equal areas above and below the centre line. This area divided by the line length is a value r_a which represents the average of the distances between the individual points and the centre line. The average of these values r_a for the 201 lines scanned is a value R_a denoting the roughness of the surface. The values obtained are also given in the table below.

	Formulation A (LAS)		Formulation B (LAS/PAS)	
	Punch surface material	Adhesion (kN)	Roughness R_a (µm)	Adhesion (kN)
40	steel *	4.7	11.3	4.3
	ptfe*	NS	10.1	2.5
	natural rubber 2mm*	NS	25.6	NS
45	moulded elastomer 2mm *	NS	45.7	NS
	moulded elastomer 8mm *	NS	28.9	NS
	silicone rubber 35µm	NS	11.6	NS
	silicone rubber 130µm	NS	17.5	NS
50	silicone rubber 170µm	NS	22.2	NS
	silicone rubber 300µm	NS	36.6	NS
				41.3

* comparative

55 [0121] It is apparent from these results that adhesion of the bar composition to steel is much greater than the adhesion with any coated punch. Therefore the recorded adhesion values for the coated punches must be the adhesion to the coated surface of the mobile punch and not the (greater) adhesion to the steel bottom plate.

[0122] With natural rubber 2mm thick, and likewise with 2mm or 8mm synthetic elastomer, the adhesion was so small

as to be indistinguishable from friction between the punch 36 and the collar 32. The value was therefore recorded as "NS" meaning "not significant".

[0123] With varying thicknesses of silicone rubber, all less than 0.5mm, the values were again too small to distinguish from friction and recorded as not significant.

5 [0124] Thus, these thin rubber coatings were effective to prevent adhesion of the bar composition to the movable punch.

[0125] With the thinner coatings, the results show a surface smoothness which was better than that obtained with the thicker coatings of natural rubber or synthetic elastomer.

10 [0126] Visual inspection also reported that the surface finish of bars moulded with the 130 micrometre silicone rubber coating was better than that of bars moulded with the punches whose surfaces were coated with the much thicker 2mm and 8mm coatings.

[0127] As mentioned earlier, a smooth surface is perceived by the consumer as being better for the fabric which is being washed.

15 EXAMPLE 2

[0128] A punch was coated with a silicone rubber coating, 30 micrometres thick, as in the previous Example.

[0129] The punch was used to make about 100 bars of each formulation. Measurements of adhesion were made, as in the previous Example, after making 27 and 100 bars of such formulation. In all cases there was no significant adhesion.

EXAMPLE 3

[0130] The following composition was prepared:

	Granulated Components	% by weight
	coconut primary alkyl sulphate	1.4
	coconut alcohol 3EO	7.6
30	coconut alcohol 6EO	4.8
	zeolite A24	29.3
	soap	2.9
	SCMC	0.8
35	sodium carbonate	0.3
	water	5.3
	Postdosed Components	
	PEG 1500	4.3
40	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

45 [0131] 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 650µm.

50 [0132] The powder was sieved to remove fine particles smaller than 180µm and large particles exceeding 1700µm. 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).

55 [0133] 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 depending on the density of the finished tablets.

[0134] Compaction of the detergent powder, to make tablets, was carried out using either plain steel top and bottom

punches, or alternatively punches which had been coated, on their faces which contact the detergent composition. The coating was polyurethane elastomer, applied by spraying. The coating thickness was in a range from 200-300 micrometres.

5 [0135] With each set of punches, two levels of force were employed, so as to produce tablets of density approximately 1140 kg/m² and 1280 kg/m².

[0136] With steel punches, 100 tablets were produced, after which the top punch was inspected. It was found to have 0.3 to 0.6g of powder firmly adhering to it, and producing indentations in the tablets surfaces.

[0137] With the coated punches, the top punch was again inspected after producing 100 tablets. It 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 10 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.

[0138] The speed of dissolution of the tablets was measured using tests as described in EP-A-466484. For tablets of the same density no difference could be detected between tablets made with coated and uncoated punches.

15 [0139] 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.

Claims

20 1. A process for the manufacture of shaped articles of compacted detergent powder by compacting a particulate composition in a mould consisting of a plurality of mould parts which are movable relative to each other, at least one of the mould parts having an elastomeric coating on a surface area which contacts the composition, **characterised in that** the elastomeric coating has a thickness of at least 5 micrometers and not exceeding 490 micrometres over more than half of the coating area.

25 2. A process according to claim 1, wherein the mould has a pair of mould parts which are movable towards and away from each other to compact the particulate composition, each of the two said mould parts having said elastomeric coating on a surface area which contacts the composition.

30 3. A process according to claim 2, wherein the mould includes a sleeve open at both ends, one of the pair of mould parts closes an end of the sleeve, and the other one of the pair of mould parts is movable into the sleeve from the other end to compact the material in the sleeve.

35 4. A process according to any one of the preceding claims, wherein each said elastomeric coating has a thickness not exceeding 490 micrometres over at least 90% of the coating area.

40 5. A process according to any one of the preceding claims, wherein the coating thickness lies in a range from 5 to 400 micrometres.

45 6. A process according to any one of the preceding claims, wherein the coating thickness lies in a range from 10 to 300 micrometres.

7. A process according to any one of the preceding claims, wherein the elastomeric material has a modulus of elasticity in the range from 0.1 to 50 MPa.

50 8. A process according to claim 7, wherein each elastomeric coating is made of a material selected from the group consisting of unsaturated carbon chain elastomers, ethylene-propylene elastomers, silicone rubbers and polyurethanes.

9. A process according to any one of the preceding claims, wherein the particulate composition contains 5 to 60% by weight of non-soap detergent active, 10 to 70% by weight of water-soluble salts and 10 to 70% by weight of water-insoluble material.

55 10. A process according to claim 9, wherein the shaped articles contain less than 15% by volume of air.

11. A process according to any one of claim 1 to 8, wherein the particulate composition contains from 5 to 50% by weight of one or more detergent-active compounds, and from 15 to 60% by weight of aluminosilicate detergency

builder.

5 12. A process according to claim 11, wherein the particulate composition contains from 1 to 8% by weight of a polymeric binder which is a water-soluble organic polymer.

10 13. A process according to any one of claims 1 to 8, 11 or 12, wherein the shaped articles contain more than 15% by volume of air.

15 14. A process according to any one of the preceding claims including a step of applying an elastomeric coating in liquid form to a mould part and allowing the coating to solidify on the mould part.

15 15. A process according to any one of the preceding claims, which includes a step of applying a fresh elastomer coating to a mould part after the mould part has been used to produce a plurality of articles, and then using the mould part to produce a further plurality of articles.

Patentansprüche

20 1. Verfahren zur Herstellung von Formgegenständen aus verdichtetem Waschmittelpulver durch Verdichten einer teilchenförmigen Zusammensetzung in einer aus einer Vielzahl von relativ zueinander beweglichen Formvorrichtungsteilen bestehenden Formvorrichtung, wobei mindestens eines der Formvorrichtungsteile eine elastomere Beschichtung auf einer Oberfläche aufweist, die mit der Zusammensetzung in Kontakt ist, **dadurch gekennzeichnet, dass die elastomere Beschichtung über mehr als die Hälfte der Beschichtungsfläche eine Dicke von mindestens 5 Mikrometern aufweist und 490 Mikrometer nicht übersteigt.**

25 2. Verfahren nach Anspruch 1, wobei die Formvorrichtung ein Paar von Formvorrichtungsteilen aufweist, die zueinander und voneinander weg beweglich sind, um die teilchenförmige Zusammensetzung zu verdichten, wobei jedes der zwei Formvorrichtungsteile die elastomere Beschichtung auf einer Oberfläche aufweist, die mit der Zusammensetzung in Kontakt ist.

30 3. Verfahren nach Anspruch 2, wobei die Formvorrichtung eine an beiden Enden offene Hülse einschließt, eines von dem Paar von Formvorrichtungsteilen ein Ende der Hülse verschließt und das andere von dem Paar von Formvorrichtungsteilen in der Hülse vom anderen Ende her beweglich ist, um das Material in der Hülse zu verdichten.

35 4. Verfahren nach einem der vorangehenden Ansprüche, wobei die elastomere Beschichtung eine Dicke aufweist, die über mindestens 90% der Beschichtungsfläche 490 Mikrometer nicht übersteigt.

40 5. Verfahren nach einem der vorangehenden Ansprüche, wobei die Beschichtungsdicke in einem Bereich von 5 bis 400 Mikrometern liegt.

45 6. Verfahren nach einem der vorangehenden Ansprüche, wobei die Beschichtungsdicke in einem Bereich von 10 bis 300 Mikrometern liegt.

50 7. Verfahren nach einem der vorangehenden Ansprüche, wobei das elastomere Material einen Elastizitätsmodul im Bereich von 0,1 bis 50 MPa aufweist.

55 8. Verfahren nach Anspruch 7, wobei jede elastomere Beschichtung aus einem Material, ausgewählt aus der Gruppe, bestehend aus Elastomeren mit ungesättigten Kohlenstoffketten, Ethylen-Propylen-Elastomeren, Silikonkautschuk und Polyurethanen, hergestellt wird.

55 9. Verfahren nach einem der vorangehenden Ansprüche, wobei die teilchenförmige Zusammensetzung 5 bis 60 Gewichtsprozent Nicht-Seifen-Waschmittelaktivstoff, 10 bis 70 Gewichtsprozent wasserlösliche Salze und 10 bis 70 Gewichtsprozent wasserunlösliches Material enthält.

55 10. Verfahren nach Anspruch 9, wobei die Formgegenstände weniger als 15 Volumen% Luft enthalten.

55 11. Verfahren nach einem von Anspruch 1 bis 8, wobei die teilchenförmige Zusammensetzung 5 bis 50 Gewichtsprozent von einer oder mehreren Waschmittelaktivstoffverbindungen und 15 bis 60 Gewichtsprozent Aluminosilikat-

Waschmittelbuilder enthält.

- 5 12. Verfahren nach Anspruch 11, wobei die teilchenförmige Zusammensetzung 1 bis 8 Gewichtsprozent eines polymeren Bindemittels enthält, das ein wasserlösliches organisches Polymer ist.
- 10 13. Verfahren nach einem der Ansprüche 1 bis 8, 11 oder 12, wobei die Formgegenstände mehr als 15 Volumen% Luft enthalten.
14. Verfahren nach einem der vorangehenden Ansprüche, einschließlich eines Schritts zum Auftragen einer elasto-10 meren Beschichtung in flüssiger Form auf ein Formvorrichtungsteil und Verfestigenlassen der Beschichtung auf dem Formvorrichtungsteil.
- 15 15. Verfahren nach einem der vorangehenden Ansprüche, das einen Schritt zum Auftragen einer frischen Elastomer-15 beschichtung auf ein Formvorrichtungsteil, nachdem das Formvorrichtungsteil verwendet wurde, um eine Vielzahl von Gegenständen herzustellen, und anschließend Verwenden des Formvorrichtungsteils zur Herstellung einer weiteren Vielzahl von Gegenständen, einschließt.

Revendications

- 20 1. Procédé de fabrication d'articles façonnés de poudre détergente compactée par compression d'une composition particulaire dans un moule comprenant plusieurs parties de moule qui se déplacent dans un mouvement relatif les unes par rapport aux autres, au moins une des parties du moule ayant un revêtement élastomère sur une aire de surface qui vient en contact avec la composition, **caractérisé en ce que** le revêtement élastomère possède une épaisseur d'au moins 5 microns et n'excédant pas 490 microns sur plus de la moitié de l'aire du revêtement.
- 25 2. Procédé selon la revendication 1, dans lequel le moule possède une paire de parties du moule qui se déplacent en se rapprochant et en s'éloignant l'une de l'autre pour comprimer la composition particulaire, chacune desdites deux parties du moule ayant ledit revêtement élastomère sur une aire de surface qui touche la composition.
- 30 3. Procédé selon la revendication 2, dans lequel le moule comprend un manchon ouvert aux deux extrémités, une des parties de la paire de parties du moule ferme une extrémité du manchon, et l'autre partie de la paire des parties du moule se déplace dans le manchon à partir de l'autre extrémité pour comprimer le matériau dans le manchon.
- 35 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel chaque revêtement élastomère possède une épaisseur n'excédant pas 490 microns sur au moins 90% de l'aire du revêtement.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'épaisseur du revêtement se situe dans un intervalle de 5 à 400 microns.
- 40 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'épaisseur du revêtement se situe dans un intervalle allant de 10 à 300 microns.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau élastomère possède un module d'élasticité compris dans l'intervalle allant de 0,1 à 50 MPa.
- 45 8. Procédé selon la revendication 7, dans lequel chaque revêtement élastomère est fait d'un matériau choisi dans le groupe comprenant les élastomères à chaînes carbonées insaturées, les élastomères éthylène-propylène, les caoutchoucs de silicone et les polyuréthanes.
- 50 9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition particulaire contient 5 à 60 % en poids de produit à action détergente sans savon, 10 à 70 % en poids de sels solubles dans l'eau et 10 à 70 % en poids de matériau insoluble dans l'eau.
- 55 10. Procédé selon la revendication 9, dans lequel les articles façonnés contiennent moins de 15 % en volume d'air.
11. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel la composition particulaire contient de 5 à 50 % en poids d'un ou plusieurs composés à action détergente, et de 15 à 60 % en poids d'adjuvant au détergent

de type aluminosilicate.

12. Procédé selon la revendication 11, dans lequel la composition particulaire contient de 1 à 8 % en poids d'un liant polymère qui est un polymère organique soluble dans l'eau.

5 13. Procédé selon l'une quelconque des revendications 1 à 8, 11 ou 12, dans lequel les articles façonnés contiennent plus de 15% en volume d'air.

10 14. Procédé selon l'une quelconque des revendications précédentes, qui comprend une étape qui consiste à appliquer un revêtement élastomère sous forme liquide à une partie du moule et à laisser le revêtement se solidifier sur la partie du moule.

15 15. Procédé selon l'une quelconque des revendications précédentes, qui comprend une étape qui consiste à appliquer un revêtement élastomère neuf à une partie de moule après l'utilisation de la partie du moule pour produire un grand nombre d'articles , et ensuite à utiliser la partie du moule pour produire un grand nombre supplémentaire d'articles.

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Fig.1.

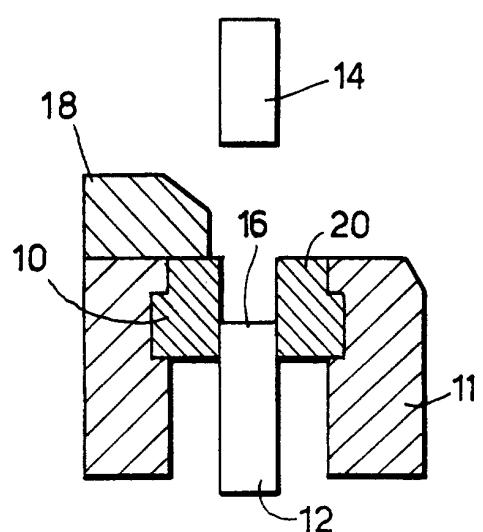


Fig.2.

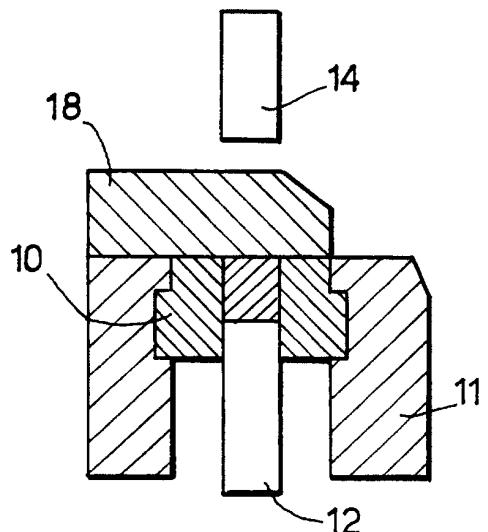


Fig.3.

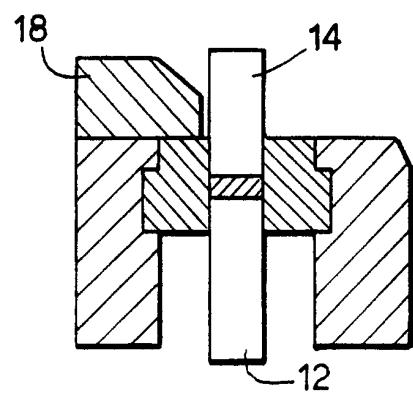


Fig.4.

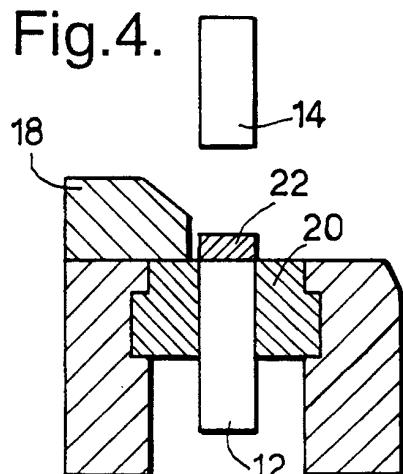


Fig.5.

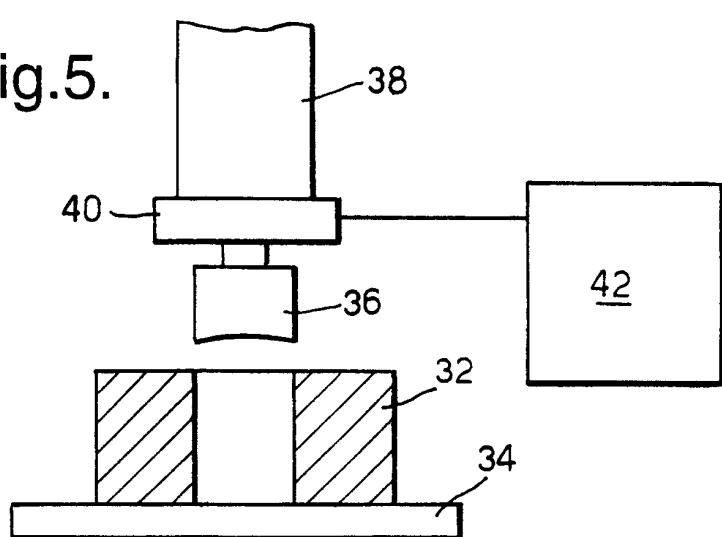


Fig.6.

