



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 354 938 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
22.10.2003 Bulletin 2003/43

(51) Int Cl.7: **C11D 17/00**, C11D 10/04,
C11D 3/32
// C11D1:22, C11D1:72

(21) Application number: **03075889.0**

(22) Date of filing: **27.03.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT SE SI SK TR**
Designated Extension States:
AL LT LV MK RO

(30) Priority: **18.04.2002 EP 02252764**

(71) Applicants:
• **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
**AT BE CH LI CZ DE DK ES FI FR GR IT NL PT SE
SK TR**
• **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB IE

(72) Inventors:
• **Bonsall, Judith Maria, R & D Port Sunlight
Wirral, Merseyside CH63 3JW (GB)**
• **Chmabers, John George, R & D Port Sunlight
Wirral, Merseyside CH63 3JW (GB)**
• **Wilson, William John, R & D Port Sunlight
Wirral, Merseyside CH63 3JW (GB)**
• **Wraige, Douglas**
Upton Chester, Cheshire CH2 1NN (GB)

(74) Representative: **Sikken, Antonius H. J. M. et al**
UNILEVER N.V.,
Patent Division,
P.O. Box 137
3130 AC Vlaardingen (NL)

(54) **Laundry tablets with improved dissolution behaviour**

(57) The invention concerns novel laundry tablets comprising granules wherein soap and surfactants are present and wherein the surfactants comprise either one or more anionic surfactants or a mix of one or more anionic and one or more non-ionic surfactants, the soap being a low water-soluble soap which is present as a

coagel with at least the anionic surfactants and wherein the soap has a Tk of at least 35°C while the weight ratio of soap to anionic surfactants is at least 0.1, preferably 0.1 to 0.5 and the weight ratio of soap to total surfactants is less than 0.5.

EP 1 354 938 A1

Description

[0001] Current laundry tablets have inferior dispersion/dissolution properties to powders because of the ability of surfactants to form viscous liquid crystalline phases during the initial stages of dilution. In a tablet format this leads to pore blockage and hence inhibition of water ingress which in turn reduces the rate of tablet break-up and dissolution.

[0002] Typically current laundry tablets contain mainly soluble surfactants such as linear alkylbenzene sulphonates (=LAS), primary alkyl sulphates (=PAS) and nonionics. It is known that the use of low levels of non-ionics prevents bleeding, whereas bleeding during storage is further prevented by the addition of a small amount of insoluble soap to the non-ionic(s). The maximum ratio of soap/non-ionic is said to be ca 0.2, preferably about 0.1 and even more preferred about 0.033 (ref WO 9842817). The soap that is present is said to aid tableting, (ref WO9842817) but higher ratios of soap/non-ionic are said to lead to unsatisfactory results.

[0003] Surprisingly we have found that incorporation of insoluble soaps into the anionic surfactant alone or in both the anionic and non-ionic surfactants in a specific form leads to superior tablet dispersion/dissolution properties.

[0004] The mechanism of this action is not clear but some scientists believe that the structuring effects of the soap on the soluble surfactants plays a role and therewith the rate of water uptake. We now found that the physical form wherein the soap and surfactants are added plays a role as well and that by careful balancing of the ratio of the low solubility soap(s) to in particular the anionic surfactant(s) and by applying a special preparation method for these blends the solubility of the blend can be designed so that negligible dissolution occurs during the initial critical stage of tablet wetting out.

Another parameter that plays a role seems the ratio of soap to total of anionic and non-ionic surfactants, while also the Tk of the soap is important. The Tk of the soap is defined as below.

The soluble-surfactant/low solubility soap particles subsequently disperse into the bulk wash solution and then dissolve.

[0005] This invention not only enhances the rate of tablet dispersion/dissolution, expressed as T90 and measured by the method disclosed e.g. in the examples of WO 00/22089, but as a result of this improvement, also reduces the risk of residues and patch damage.

[0006] Tablets that comprise low solubility soap and anionics in ratios of about 0.1 are disclosed in e.g. US 5 900 399 (examples 1 and 2); in EP 716 144 (examples) tablets are disclosed wherein the ratio between a non specified soap and anionics ranges from about 2.3 to about 0.4, while the ratio between the soap and the total of anionics and non-ionics herein is about 0.1 to 0.2. Still these tablets do not display satisfying dissolution properties. This is due, as we found, to the fact that the soap and anionics are not added in the correct physical form. We found that if first a coagel is made from at least the anionics (but the non-ionics can be present as well) and the low solubility soap and this coagel is added to the tablets the dissolution properties improved considerably.

[0007] A coagel is defined here as a thermoreversible gel, which is formed by spontaneous separation of an anisotropic interconnected solid network from an isotropic continuum. These structures provide high gel-strengths with relatively low solids content, due to their high degree of interconnectivity (cf Cahn c.s in J Chem Phys 31, 1959 p. 688 and 42, 1965, p 93)

[0008] One way to make a coagel of these ingredients is to contact a mix of solid carrier material, in particular a mix of zeolite and soda ash with at least part of the free fatty acid constituents of the low solubility soap and the acidic form of anionic surfactants (optionally in the presence of non-ionic surfactants) and then neutralise the acids by an in-situ neutralisation reacting the soda ash which is part of the carrier material with the acids. In fact we prefer to make the coagel by an in-situ neutralisation of a mix of at least the anionics and the free fatty acid constituents of the soap using an alkali reagent.

Therefore our invention concerns in the first instance novel laundry tablets comprising granules wherein soap and surfactants are present and wherein the surfactants comprise either one or more anionic surfactants or a mix of one or more anionic and one or more non-ionic surfactants and wherein the soap has a Tk of at least 35°C while the weight ratio of soap to anionic surfactants is at least 0.1, preferably 0.1 to 0.5 and the weight ratio of soap to total surfactants is less than 0.5.

The soap can be present as a coagel with the anionics only but also coagels of soap and all surfactants present lead to good results. The laundry tablet so-formed has enhanced dispersion/dissolution properties while maintaining tablet integrity. This integrity can be expressed as Fmax, which is measured by the method disclosed in the examples of WO 00/22089

[0009] Very convenient soaps are soap derived from one or more fatty acids selected from the group consisting of straight chain fatty acids with 12 to 24 carbon atoms.

The "low solubility soap" is defined by its solubility in water expressed as a Kraft temperature, (Tk value, i.e. the minimum solubility temperature for the soap corresponding to the crystal solubility boundary). The target minimum value for this Tk is 35°C. Examples of suitable soaps include those selected from one or more of saturated and unsaturated alkyl carboxylates where the counterion is one of sodium, potassium, calcium or magnesium. The soap or blend must have a Tk value in excess of 35 Celsius. Examples of single soaps include sodium laurate, sodium myristate, sodium palmi-

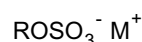
tate, sodium stearate, sodium behenate, potassium palmitate, potassium stearate and calcium laurate. Examples of blends include blends from 99/1 to 1/99 of sodium soaps of palmitate and myristate, palmitate and stearate, and myristate and stearate. Examples of blends containing unsaturated alkyl soaps include less than 1:1 blends of sodium oleate and sodium stearate and sodium oleate and sodium palmitate.

[0010] Other components can also be post dosed to the compositions. Preferred additional components are urea and sodium carbonate. Other components include one or more detergency builders, bleaches, bleach precursors and optionally other detergent ingredients.

[0011] The soluble surfactants are usually comprised of one or more anionic and nonionic surfactants but can also include amphoteric and cationic surfactants. Typically the anionic surfactant is selected from LAS and PAS. Typically the nonionic surfactants are selected from alcohol ethoxylates. The amphoteric surfactants are typically betaine-type derivatives.

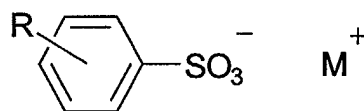
[0012] Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkyl benzene sulphonates (= LAS), particularly sodium linear alkyl benzene sulphonates having an alkyl chain length of C₈-C₁₅; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0013] Primary alkyl sulphate (= PAS) having the formula:



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 surfactant.

[0014] 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 surfactant.

[0015] Suitable nonionic surfactant 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.

[0016] Specific nonionic surfactant compounds are alkyl (C₈₋₂₂) phenoethylene oxide condensates, the condensation products of linear or branched aliphatic C₈₋₂₀ primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine.

[0017] Especially preferred are the primary and secondary alcohol ethoxylates, especially the C₉₋₁₁ and C₁₂₋₁₅ primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

[0018] The coagel of soluble and insoluble surfactants necessary for the invention can also be made by a process wherein the in-situ neutralisation of the acids is performed by using an alkali reagent of a co-injected mix of anionic surfactants and the free fatty acid constituent of the soap during an NTR processing.

[0019] The granules that can be applied can be the result of a spray drying process.

[0020] The preferred process for the preparation of our novel laundry tablets involves the following steps:

- first granules are made by a process wherein solid carrier material, in particular a mix of zeolite and soda ash is contacted with at least part of the free fatty acid constituents of a low solubility soap and the acidic form of anionic surfactants, optionally in the presence of non-ionic surfactants
- whereupon the acids are neutralised in -situ by reacting with the soda ash which is part of the carrier material
- the coagel so obtained is mixed with the other components of the tablet
- and the tablet is formed by compressing a premoulded amount of granules

[0021] According to a preferred embodiment the neutralisation reaction between acids and soda ash is performed in a high shear solid mixer.

[0022] Other tablet components typically include builders, bleaches, bleach precursors, optical brighteners, polymers, electrolytes, fillers, organic disintegrants and clays

The following examples illustrate the invention:

Example 1: Control product

[0023] In this example of a control product, the insoluble sodium soap, (1:1 blend of C16 and C18 fatty acids which are subsequently neutralised during processing) is mixed with the nonionic surfactant to prevent bleeding on storage. No soaps are blended with the anionic surfactant. The ratio of insoluble soap/ nonionic surfactants is ca 1.6/10, and the ratio of insoluble soap/total soluble surfactants is 0.7/10.

Process details; All powders (except Zeolite A24 layer) added to FS100 batch high shear granulator. Powders premixed. The LAS acid is heated to approx 70°C and added to the powder.

The nonionic (7EO plus 3EO) / fatty acid mixture, (ratio nonionic/soap = 1.6/10) is heated to approx. 70°C and is poured into the mixer. Following granulation the mixer is stopped and the layer is then added onto the top of the granules. The mixer is started and the product is discharged. Base powder was sieved and the cut used was 850-1400µm. This base powder was then mixed with post-dosed ingredients to give the full formulation of Table 2.

Table 1:

Control product - (wgt%)	
Formulation	Control
LAS Acid	18.67
NI 7eo	5.93
NI 3eo	3.11
Pristerine 4916 (A fully hardened tallow fatty acid soap)	1.46
Na Acetate	5.93
Light Soda Ash (LSA)	12.64
Sodium carboxymethyl Cellulose (SCMC)	0.88
Zeolite A24	48.76
Zeolite Layer	2.63

Table 2:

Full formulation details (wgt %)	
Formulation	Control
Base Powder	46.40
Anti foam granule	1.80
NaPercarbonate	15.00
Tetraacetyl ethylene diamine (TAED)	5.10
Anti redeposition polymer	5.50
NaCarbonate dense	1.40
NaAcetate	24.90

[0024] The gross tablet properties of hardness, (expressed as Fmax) and solubility, (expressed as T90) are shown in Table 3.

Table 3:

Target Fmax for tablets 35N (i.e. Day 0 value)		
Control		
Time (week)	Fmax	T90
0	36.1	248.2
1	35.38	271.52
4	34.29	250.2

[0025] Example 2: This product contains a blend of insoluble sodium soap, (derived from C14 fatty acid) blended with the anionic surfactant, (LAS) with a soap/LAS ratio = ca 1.6/10 and a soap/total soluble surfactant, (LAS + Nonionic) ratio = 1/10. In this product, no soap is present in the nonionic surfactants. The base detergent formulation is given in Table 4.

Table 4 -

(wgt %)	
Formulation	
LAS Acid	18.4
NI 7eo	5.8
NI 3eo	3.0
Na Acetate	5.8
LSA	12.4
SCMC	0.9
Myristic acid 2914	2.8
Zeolite A24	48.2
Zeolite A24 layer	2.6

[0026] Process details; All powders (except Zeolite A24 layers) added to FS100 batch high shear granulator. Powders premixed. The LAS acid and merits acid mixture is heated to approx. 70°C and added to the powder. The nonionic (7EO plus 3EO) mixture is heated to approx. 70°C and is poured into the mixer. Following granulation the mixer is stopped and the layer is then added onto the top of the granules. The mixer is started and the product is discharged. Base powder was sieved and the cut used was 850-1400µm.

[0027] Full formulation details (wet %) after addition of post-dosed ingredients are given in Table 5.

Table 5:

Formulation	Control
Base Powder	46.40
Anti foam granule	1.80
NaPercarbonate	15.00
TAED	5.10
Anti redeposition polymer	5.50
NaCarbonate dense	1.40
NaAcetate	24.90

[0028] This powder was subsequently tabletted to a target hardness of 35 Newton's. The gross tablet properties are given in Table 6.

EP 1 354 938 A1

Table 6:

2.5% Myristate in LAS I		
Time (week)	Fmax	T90
0	30.0	213.9
1	33.05	237.62
4	33.20	208.5

[0029] Comparison of the gross tablet properties of this product and the control product of Example 1 shows that this product has similar hardness but faster dissolution time.

[0030] Example 3 - this product contains C14 soap, (myristate) blended in with both LAS and nonionics. The ratio of soap/LAS= 0.8/10 and the soap/nonionics = 2/10. The ratio of soap/total soluble surfactants = 1/10. The base detergent formulation is given in

Table 7:

(wgt %)	
Formulation	
LAS Acid	16.64
NI 7eo	5.27
NI 3eo	2.73
Myristate 2914	2.55
Na Acetate	5.27
LSA	11.27
SCMC	0.73
Zeolite A24	53.18
Zeolite Layer	2.36

[0031] Process details; All powders (except Zeolite A24 layer) added to FS100 batch high shear granulator. Powders premixed. The LAS acid and half of the myristic acid mixture is heated to approx 70°C and added to the powder. The nonionic (7EO plus 3EO) containing the remaining half of the myristic acid is heated to approx. 70°C and is poured into the mixer. Following granulation the mixer is stopped and the layer is then added onto the top of the granules. The mixer is started and the product is discharged. Base powder was sieved and the cut used was 850-1400µm.

Full formulation details (wgt %)	
Formulation	Control
Base Powder	46.40
Anti foam granule	1.80
NaPercarbonate	15.00
TAED	5.10
Anti redeposition polymer	5.50
NaCarbonate dense	1.40
NaAcetate	24.90

EP 1 354 938 A1

Target Fmax for tablets 35N (i.e. Day 0 value)		
2.5% Myristate in LAS and NI		
Time (week)	Fmax	T90
0	33.80	220.70
1	36.20	227.10
4	35.44	236.0

[0032] Comparison of the gross tablet properties of this product and the control product of Example 1 show this product to have similar hardness but faster dissolution time.

[0033] Example 4 - this product contains C14 soap, (myristate) blended in with both LAS and nonionics. The ratio of soap/LAS= 2/10 and the soap/nonionics = 4/10. The soap/total soluble surfactant ratio = 2.7/10. The base detergent formulation is given in Table 8.

Table 8:

(wgt %)	
Formulation	
LAS Acid	14.56
NI 7eo	4.63
NI 3eo	2.37
Myristate 2914	5.60
Na Acetate	4.20
LSA	8.87
SCMC	0.57
Zeolite A24	55.21
Zeolite Layer	3.99

[0034] Process details; All powders (except Zeolite A24 layer) added to FS100 batch high shear granulator. Powders premixed. The LAS acid and half of the myristic acid mixture is heated to approx 70°C and added to the powder. The nonionic (7EO plus 3EO) containing the remaining half of the myristic acid is heated to approx. 70°C and is poured into the mixer. Following granulation the mixer is stopped and the layer is then added onto the top of the granules. The mixer is started and the product is discharged. Base powder was sieved and the cut used was 850-1400µm.

Table 9

Full formulation details (wgt %)	
Formulation	Control
Base Powder	46.40
Anti foam granule	1.80
NaPercarbonate	15.00
TAED	5.10
Anti redeposition polymer	5.50
NaCarbonate dense	1.40
NaAcetate	24.90

EP 1 354 938 A1

Table 10

Target Fmax for tablets 35N (i.e. Day 0 value)		
5% Myristate in LAS and NI		
Time (week)	Fmax	T90
0	25.20	132.20
1	28.94	146.44
4	27.20	139.40

[0035] Comparison of the gross tablet properties of this product and the control product of Example 1 show this product to have similar hardness but faster dissolution time.

[0036] Example 5: In this product we have used C14 soap to structure the LAS and nonionics with soap/LAS ratio = 3.8/10 and soap/nonionic ratio = 8/10. The ratio of soap/total soluble surfactants = 5.1/10.

The base detergent formulation is given in Table 11.

Table 11:

Formulation	
LAS Acid	12.93
NI 7eo	4.12
NI 3eo	2.15
Na Acetate	4.12
LSA	8.71
SCMC	0.56
Myristate 2914	9.37
Zeolite A24	54.11
Zeolite Layer	3.93

[0037] Process details; All powders (except Zeolite A24 layer) added to FS100 batch high shear granulator. Powders premixed. The LAS acid and half of the myristic acid mixture is heated to approx 70°C and added to the powder. The nonionic (7EO plus 3EO) containing the remaining half of the myristic acid is heated to approx 70°C and is poured into the mixer. Unfortunately at this high level of incorporation of myristic acid it was not possible to produce an acceptable base powder due to the high liquids content prior to neutralisation. This example thus illustrates that there is maximum level of soap that can be incorporated in the tablets.

Examples 6A and 6B

[0038] In these products we have made the control formulation of Example 1 to a different tablet hardness and coded this product 'Example 6A'. In addition we have made a further product, 'Example 6B' by using a soluble soap blend, (sodium oleate/sodium linoleate) to structure the LAS and nonionics with soap/LAS ratio = 1.9/10 and soap/nonionic ratio = 4.1/10 in Example 6B. This soap blend falls outside the scope of the requirement that the Tk of the soap being >35°C. The actual Tk of the sodium soap of Priolene 6930 will be ca 15°C.

The base detergent formulation for Example 6B is given

Table 12

Formulation	
LAS Acid	14.56
NI 7eo	4.63
NI 3eo	2.37

EP 1 354 938 A1

Table 12 (continued)

Formulation	
Priolene 6930	5.60
Na Acetate	4.20
LSA	8.87
SCMC	0.57
Zeolite A24	55.21
Zeolite Layer	3.99

[0039] Process details; All powders (except Zeolite A24 layer) added to FS100 batch high shear granulator. Powders premixed. The LAS acid and half of the priolene fatty acid mixture is heated to approx. 70°C and added to the powder. The nonionic (7EO plus 3EO) containing the remaining half of the priolene acid is heated to approx. 70°C and is poured into the mixer. Following granulation the mixer is stopped and the layer is then added onto the top of the granules. The mixer is started and the product is discharged. Base powder was sieved and the cut used was 850-1400µm.

Full formulation details (wgt %)	
Formulation	Control
Base Powder	46.40
Anti foam granules	1.80
NaPercarbonate	15.00
TAED	5.10
Anti redeposition polymer	5.50
NaCarbonate dense	1.40
NaAcetate	24.90

Fmax and T90 data:		
	Control (6A)	Product 6B
Fmax (N)	22	18
T90 (s)	120	120

[0040] Comparison of the gross tablet properties of these products show that the product 6B made at similar hardness to the control product has an identical dissolution time. Hence use of the soluble soap has not delivered any improvement in dissolution properties

[0041] Examples 7 and 8: In these examples the control base powder of example 1 is made and the postdose ingredients, are as shown in Table 13 with the Fmax values as given.

Table 13

Formulation

Base 1 (1.5% pristerine)	50%
Acetate or urea	30%
Ash	20%

Acetate variant		
Time	Fmax N	T90s
2 days	32.5	275

Urea variant		
Time	F max N	T 90 sec
2 days	51.6	230

[0042] The T90 values are clearly superior when the sodium acetate is replaced by urea, even though the tablet hardness is greater in the urea containing tablet.

[0043] Example 8: In this example the base powder of Example 2 has been used with the post dose ingredients as shown in Table 14.

Table 14:

Formulation

Base 2 (2.8% myristate in LAS)	50%
Urea	30%
Ash	20%

Time	Fmax N	T90 sec
2 days	47.5	160

[0044] The T90 values are substantially shorter than those of Example 7 where an identical post-dose was used. This confirms that the combination of modified base and urea.soda ash post dose work together to deliver a further improvement in dissolution.

[0045] Example 9: In this example the base powder of Example 3 has been used with the postdose ingredients as shown in Table 15.

Table 15

Formulation

Base 3 (2.5% myristate in LAS+NI)	50%
Urea	30%
Ash	20%

Time	F max N	T90 sec
2 days	49.6	155

[0046] As in the previous example the combination of modified base and selected post dose ingredients provides a combined decrease in T90, i.e. improved dissolution relative to the conventional base of Example 7.

[0047] Example 10: In this example the base powder of Example 4 has been used with the postdose ingredients as shown in Table 16. The T90 value is less than that of Example 7 where the conventional base is used.

Table 16

Formulation

Base 4 (5.6% myristate in LAS+NI	50%
Urea	30%
Ash	20%

Time	F max N	T90 sec.
2 days	57	165

Table 16 = base of EG4 + urea/soda ash

Claims

1. Laundry tablet comprising granules wherein soap and surfactants are present and wherein the surfactants comprise either one or more anionic surfactants or a mix of one or more anionic and one or more non-ionic surfactants, the soap being a low water-soluble soap which is present as a coagel with at least the anionic surfactants and wherein the soap has a Tk of at least 35°C while the weight ratio of soap to anionic surfactants is at least 0.1, preferably 0.1 to 0.5 and the weight ratio of soap to total surfactants is less than 0.5.
2. Laundry tablet according to claim 1 wherein the soap is present as a coagel with all surfactants.
3. Laundry tablet according to claims 1 and 2 wherein the coagel of soap and surfactants is the result of an in-situ neutralisation of a mix of at least the anionic surfactants and the free fatty acid constituents of the soap using an alkali reagent.
4. Laundry tablet according to claims 1 to 3 wherein the soap is derived from one or more fatty acids selected from the group consisting of straight chain fatty acids with 12 to 24 C-atoms.
5. Laundry tablet according to claims 1 to 4 wherein the coagel of soap and surfactants is present in the form of granules which have a soap content of maximum 10 wt %.
6. Laundry tablet according to claims 1 to 5 wherein the granules are the result of a spray drying process.

EP 1 354 938 A1

7. Laundry tablet according to claims 1 to 6 wherein the tablets contain post dosed ingredients in particular urea and soda ash.

5 8. Process for the preparation of laundry tablets with the composition according to claims 1 to 7 wherein tablets are made by a process wherein first granules are made by a process wherein solid carrier material, in particular a mix of zeolite and soda ash is contacted with at least part of the free fatty acid constituents of a low solubility soap and the acidic form of anionic surfactants, optionally in the presence of non-ionic surfactants whereupon the acids are neutralised in-situ by reacting with the soda ash which is part of the carrier material to form a coagel whereupon the other components of the tablet are added and the tablets are formed by compressing a premoulded amount of granules

10 9. Process according to claim 8 wherein the neutralisation reaction between acids and soda ash is performed in a high shear solid mixer.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 07 5889

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	EP 0 716 144 A (UNILEVER) 12 June 1996 (1996-06-12) * page 4, line 23-42 * * examples 1,2 * ---	1-9	C11D17/00 C11D10/04 C11D3/32 //C11D1:22, C11D1:72
D,A	US 5 900 399 A (STEVERMANN BIRGIT ET AL) 4 May 1999 (1999-05-04) * column 6, line 22 - column 8, line 11 * * examples 1,2 * ---	1-9	
A	GB 1 004 596 A (PROCTER & GAMBLE) 15 September 1965 (1965-09-15) * page 2, line 49-108 * * examples * ---	1,8	
A	US 6 083 893 A (ZINT DAVID ROBERT ET AL) 4 July 2000 (2000-07-04) * column 1, line 55 - column 2, line 63 * * examples; table 2 * -----	1,8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 July 2003	Examiner Bertran Nadal, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03 B2 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 07 5889

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-07-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0716144	A	12-06-1996	EP	0716144 A2	12-06-1996
			US	5916866 A	29-06-1999
US 5900399	A	04-05-1999	DE	4404279 A1	17-08-1995
			AT	200794 T	15-05-2001
			DE	59509220 D1	31-05-2001
			WO	9521908 A1	17-08-1995
			EP	0743978 A1	27-11-1996
			EP	0965565 A1	22-12-1999
			ES	2157320 T3	16-08-2001
GB 1004596	A	15-09-1965	BE	628622 A	
			DK	106563 A	
			FR	1348321 A	04-01-1964
			NL	289572 A	
US 6083893	A	04-07-2000	CA	2147674 A1	17-11-1995
			TR	28777 A	03-03-1997

EPO FORM P0469

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82