

The present invention relates to finely divided material of natural shells and/or kernels treated with a bleaching agent, in particular hydrogen peroxide, which is comprised in cosmetic products as an abrasive, to a process for its production and to uses of the abrasive.

An important component of cosmetic cleansing agents and preparations is the abradant which has the function of mechanically supporting the cleaning action of detergent or surface-active components.

According to the state of the art, a variety of inorganic and organic materials may be used as mechanical cleaning agents and remedies in cleansing preparations, e.g., in hand cleaning agents or so-called peeling creams and special cleaning gels for the removal of the uppermost, dead skin cells or of skin impurities, e.g., of the face or other parts of the body.

EP-B-01 04 679 discloses an abrasive material consisting of agglomerates of finely divided grinding material agglomerated by means of an organic binder; calcite is used as abrasive. Numerous other abrasive materials are known, for example, chalk, marble, dolomite, feldspar, or quartz. Owing to their strong abrasive action these materials are unsuitable for many applications. According to said patent, the calcite which is agglomerated in very fine distribution with a hydrophobic organic binder avoids scratching of sensitive surfaces.

The addition of a chlorine-forming bleach is mentioned in Example 4 wherein the chlorine supports the cleaning action of the abrasive and, if used to clean plastic surfaces, has a germicidal action.

US-A-2561043 relates to a special device in which, amongst others, nutshell flours may be produced from nutshells without the danger of explosions or fire during grinding.

By this, a nutshell flour of < 325 mesh (mesh size $45\ \mu\text{m}$) may be produced from nutshells at a working temperature of the device of up to 275°F (corresponding to 135°C) by cooling the mill work with 0.1 to 0.5 gallons (corresponding to 0.4 to 1.9 liters) of water per minute. The residual moisture of this nutshell flour amounts to 2 to 4%.

US-A-4279890 relates to powder compositions comprising walnut shell flour and having a good absorption of body fluid; it relates in particular to facial powder compositions. The walnut shell flour, the production of which is not explained in greater detail, is used in the form of a powder having a particle size of less than $40\ \mu\text{m}$, preferably of less than $30\ \mu\text{m}$, which - according to the statements in this prior art publication - is a compelling size to recognize its properties as a filler and oil-absorbing agent. The content of the walnut shell flour in the cosmetic compositions amounts to between 30 and 99%, the rest consisting of other oil and/or moisture-absorbing fillers, binders, and other auxiliary materials and additives.

US-A 4,407,789 (E: Eigen et al.) describes a high absorption body powder composition mainly consisting of finely ground rice hulls which pass through a 200 mesh sieve as base powder, in amounts up to 98%-wt. of the composition and from 1 up to 15%-wt. of the total composition of a suitable binding agent which is selected from the group consisting of zinc, magnesium and aluminum stearate. Thus the object of this U.S.-patent is to provide a body powder composition of high absorbency and to provide such a composition which approximates the skin color to a great extent. The

very great absorption capacity of dried rice hulls is especially mentioned in column 2, lines 41 to 44. Except for the indication in column 2 bridging column 3 that the rice hulls are to be ground as finely as possible, there are no additional hints as to a special treatment of this rice hull flour, i.e., the teaching of this U.S.-patent does not render obvious the fact to bleach the shells prior to their use.

Japanese patent application No. J 611 59 495 discloses a cleaning composition comprising polysaccharide and ethylene-maleic-anhydride-copolymer; as abrasive agents it includes SiO_2 , Al_2O_3 , MgO , SiC , B_4C , Fe_2O_3 , TiO_2 and others, as well as additives, such as perfume, dyes, fungicidal agents, rust inhibitors, bleaches, and pH-controlling agents.

Similar abrasives are described in Japanese patent application No. J 59 036 200.

To exclude the risk of an excessive abrading action of inorganic materials, wood flour has been introduced as abrasive in cosmetic products (Haut und Beruf, Strategien zu berufsbedingten Hauterkrankungen, H. Tronnier, Grosse-Verlag, Berlin 1989, pages 84/85).

However, it has been known for long that wood dust may have detrimental effects on the skin and the respiratory system due to components acting as allergens. Examples of wood components injurious to health include resins, terpenes, phenols, tannins, and quinones.

Other products use a light wood flour which is free of resin and barks, this flour is said to comprise smaller amounts of possible allergenic accompanying substances (Humane Produktion, 7/88,

pages 8 and 9, Fair Report on the 9th Trade Exhibition: Arbeitssicherheit [Industrial Safety] in Hannover).

A skin cleansing paste comprising as abrasives light wood flour and granular material of mainly untreated olive kernels is described in an advertisement of Chemische Fabrik Wilden GmbH, P.O.Box 10 11 80, 6078 Neu-Isenburg 1, Germany.

However, wood flour has a high germ content and, as a result of its soft, fibrous structure, swelling processes in the final product occur, resulting in an undesired viscosity increase and, as a consequence, in application technological disadvantages. In addition, about 2%-wt. of brightening pigments, e.g., titanium dioxide, have to be added to obtain bright, clean-looking and cosmetically acceptable products.

These disadvantages of wood meal are cleared up by using abrasives based on polyethylene or polyurethane powder. However, the shortcoming of plastic powders is the fact that they are not biodegradable and in several instances result in an irregular particle size distribution due to difficult milling processes. Thus - also caused by the low powder density of these materials - problems with respect to formulation occur in the production of cosmetic products.

Natural abrasives, such as washed and ground walnut shells, as well as ground apricot stones or olive kernels have been introduced as materials which, based on their hardness and grain size, are suitable for superficial skin cleansing. Although these materials are treated with germicides, the maximum number of organisms amounts to about 200/g (see, for example, folder of Cosmetochem AG, Riedstraße 7, CH-6330 Cham, Switzerland).

These materials have a gentle, excellent cleaning action and do not scratch the skin. However, like polyurethane powders, they result in cosmetic products having a dark and dirty appearance. Consequently, as in the case of wood flour, brightening pigments, e.g., titanium dioxide, have to be added in an amount of about 2% by weight.

A bleaching process for shells of walnuts is described in Research and Industry, Volume 29, March 1984, pages 10-16.

A treatment with sodium hydrogensulfite and other materials shall improve the appearance of the shells to facilitate the export of the walnuts from India to Europe.

The mentioned state of the art makes it clear that there is still an urgent need for an abrasive that - with the lowest possible concentration or even complete omission of brightening substances - results in optically bright and cosmetically acceptable, clean products when used in cosmetic cleaning agents. It is to be a natural product with a germ content below 100/g and a minimum of allergenic substances; in addition, it must be biodegradable and shall exhibit a defined, constant particle size distribution.

It is the object of the present invention to provide an abrasive for cosmetic products.

This object is achieved by a specially obtained and composed abrasive substance. Thus, the present invention relates to an abrasive for cosmetic preparations which may optionally comprise surfactants, soaps or other emulsifiers, organic solvents or oils, as well as thickeners, builders, re-greasing agents, perfumes, preservatives, dyes and antioxidants, if required, which is

characterized by the fact that it comprises bleached, natural shell and/or kernel flour.

Another object of the present invention is to provide a process for the manufacture of said abrasive characterized in that natural shells and/or kernels are ground into a flour of a defined grain size, the flour is treated with a bleaching agent in hydrous suspension, then filtered off and finally washed with water and dried.

Yet another object of the present invention is to use said abrasive in skin cleaning agents. Still a further object of the present invention is to provide cosmetic preparations, in particular hand washing and hand cleansing agents, comprising the above abrasive.

The preferred bleaching agent is aqueous hydrogen peroxide solution. According to the present invention the production of the abrasive is characterized by grinding natural shells and/or kernels into a flour of a defined particle size distribution, treating the flour in aqueous suspension with a bleach, followed by filtering it off and washing and drying it.

According to the present invention the abrasive is used, for example, in solventless or solvent-containing hand cleaning pastes, anhydrous skin cleansing agents and peeling creams.

The natural shell and/or kernel flour may, for example, be that of walnut shells, almond shells, hazelnut shells, olive kernels, apricot stones, cherry stones, or other natural shell or kernel flours, e.g., that of palm kernels and coconuts, pistachio nut and pine-nut shells and other pomaceous fruit, as well as any mixture of the named materials.

To obtain a product having the desired particle size distribution, the shell and/or kernel material is ground into a flour in a manner known per se, optionally including screening, with the particle size

amounting to 50 to 2000 μm , preferably 70 to 1000 μm , and in particular 80 to 400 μm .

The known comminuting machines or mills may be used for grinding, examples thereof include: impact mills with pendulum or plate impact, grind rolling mills, hammer or pinned disk mills, optionally with classifier units, e.g., Condux-mills. In a stirrer vessel, at a temperature of 20°C to 100°C, preferably of 50°C to 100°C, the flour is then treated, e.g., with an aqueous solution of hydrogen peroxide used as bleach within a period of 30 to 300 minutes, preferably 60 to 90 minutes. The concentration of the hydrogen peroxide amounts to 1.0%-wt. to 10.0%-wt., preferably 1.0%-wt. to 3.0%-wt., relative to the total initial charge. Preferably, the bleach, e.g., the hydrogen peroxide, is used in combination with a stabilizer during the bleaching treatment. If the bleaching is effected with hydrogen peroxide, examples of suitable stabilizers include soda water glass, magnesium chloride, carboxylic acids, and phosphoric acids as well as chelating agents and polyacrylic acid and/or the salts thereof.

Residues of H_2O_2 may optionally be destroyed by reducers, e.g., sodium hydrogensulfite or ascorbic acid, or by increasing the temperature of the suspension to 100°C.

Subsequently, the flour is filtered off and washed with water to remove residues of water-soluble impurities. The product thus obtained is dried at 100°C to 170°C, preferably at 120°C to 150°C, or under vacuum within a temperature range of 60°C to 140°C, up to a residual moisture content of 10% by weight, preferably 0.2 to 8.0%-wt.

The dry product may now be used in various cosmetic preparations. The use in skin cleansing agents, however, is a particularly suitable application.

Surprisingly, bright, clean and cosmetically acceptable pastes may be obtained with such a bleached natural flour, and titanium dioxide may completely be omitted or used in an amount of only 0.5%-wt. Whereas - prior to bleaching - the natural flours exhibit germ contents of 10^3 to 10^4 /g and sometimes even more, the bleaching treatment and drying process result in germ contents of clearly below 10^2 /g. Thus, the amount of preservatives to be used in the final product can be minimized, reducing the risk of an allergisation caused by preservatives. The content of undesired accompanying substances in the flour is reduced by the bleaching and washing procedure. The bleached flours are completely biodegradable and present in a defined and constant particle size distribution. Connected with a higher rigidity, as compared to that of the wood flour, the uniform grain size distribution allows to achieve a viscosity which is appropriate for hand cleaning pastes, without swelling processes taking place.

The examination of bleached walnut shell flour with respect to sensitising effects did not indicate an activation of the immunologic system. Thus, one may not expect that, in the case of human exposure, there will be an allergenic potential after dermal contact.

The following examples will illustrate the process for the manufacture and the use of the abrasive according to the present invention.

Example 1

Bleaching of natural shell or kernel flour with hydrogen peroxide.

The bleaching process is carried out in a 1000-liter-alloy steel apparatus equipped with multistage impulse counter-current agitator, heating and cooling device. The starting preparation amounts to 518.3 kg.

300.0 kg	water
150.0 kg	walnut shell flour, mean grain size 100 - 200 μm
26.3 kg	sodium hydroxide solution, 45%
3.0 kg	soda water glass and
3.0 kg	magnesium chloride

are placed in the reactor vessel.

The dark brown suspension is heated to 60°C under constant stirring. 26.3 kg hydrogen peroxide (35%) are added continuously within a period of 30 minutes. After half of the addition, the suspension changes its color from dark brown to beige. To complete the reaction, stirring is continued for 90 minutes, and the residual hydrogen peroxide content is determined by titration.

In order to reduce the excessive hydrogen peroxide, the equimolar amount of ascorbic acid or sodium sulfite may be added, or the decomposition is achieved by heating to 90 to 100°C.

The suspension is filtered over a chamber filter press, and the filter cake is washed with hot water. Subsequently, the water content amounts to about 50%.

The moist natural flour is then dried in a moving stream dryer up to a residual water content of 5.1%. A disk dryer may also be used.

The yield amounts to about 95%, relative to the flour employed.

In said dry condition, the bleached flour can be stored for several weeks and months without spoiling microbially. It may directly be used in hand cleaning pastes.

Example 2

When the technical process had been optimized, the amount of the employed magnesium chloride could be reduced by 50% and that of the added hydrogen peroxide by 21.6%. Thus, with a total initial charge of 518.3 kg, only 1.5 kg magnesium chloride and only 20.6 kg hydrogen peroxide (35%) are necessary to achieve the same bleaching result.

An additional improvement of the bleaching process was achieved by substituting the stabilizers soda water glass and magnesium chloride by phosphoric acid and by carrying out the process at room temperature. The remaining hydrogen peroxide is washed out with the washing water, or it is destroyed during the drying process. The advantages are: saving of process time, energy cost and raw material cost. The portion of hydrogen peroxide needed for the reaction could be reduced once again by 25%, relative to the starting concentration.

Examples 3 to 6 relate to a solventless and a solvent-containing formulation of a hand cleaning paste according to the present invention, to a formulation of a solventless hand cleaning paste without TiO_2 or with only a small portion of TiO_2 and preservative, as well as to an anhydrous skin cleansing agent and a peeling cream with bleached flour of shells and/or kernels.

Example 3

Formulation of a solventless hand cleaning paste.

Raw material	Amount used/ %-wt.
surfactant combination consisting of sodium lauryl sulfate and sodium alkylbenzene sulfonate, 50%	18.00
castor oil sulfonate, 68%	10.00
water	51.30
citric acid	0.30
carboxymethylcellulose	1.00
olein	2.00
titanium dioxide	2.00
bleached shell or kernel flour, e.g., walnut shell flour, < 350 μ m	15.00
hexamethylenetetramine	0.20
perfume	0.20
	100.00

Example 4

Formulation of a solventless hand cleaning paste with a small proportion of titanium dioxide and preservative.

Raw material	Amount used/ %-wt.
surfactant combination consisting of sodium lauryl sulfate and sodium alkylbenzene sulfonate, 50%	18.00
castor oil sulfonate, 68%	10.00
water	52.97

citric acid	0.30
carboxymethylcellulose	1.00
olein	2.00
titanium dioxide	0.50
bleached shell or kernel flour, e.g., walnut shell flour, < 250 μm	15.00
2-bromo-2-nitropropane-1,3-diol	0.03
<u>perfume</u>	<u>0.20</u>
	100.00

Example 5

Formulation of a solventless hand cleaning paste without titanium dioxide portion.

Raw material	Amount used/ %-wt.
surfactant combination consisting of sodium lauryl sulfate and sodium alkylbenzene sulfonate, 50%	18.00
castor oil sulfonate, 68%	10.00
water	53.47
citric acid	0.30
carboxymethylcellulose	1.00
olein	2.00
bleached shell or stone flour, e.g., olive kernel flour, < 400 μm	15.00
2-bromo-2-nitropropane-1,3-diol	0.03
<u>perfume</u>	<u>0.20</u>
	100.00

Example 6

Formulation of a solvent-containing hand cleaning paste.

Raw material	Amount used/ %-wt.
sodium monoethanolamine	
fatty alcohol sulfate, 40%	37.00
castor oil sulfonate, 68%	14.00
water	11.97
citric acid	0.30
carboxymethylcellulose	2.00
n-paraffin	19.00
silicon dioxide	0.50
bleached shell or kernel flour, e.g., walnut shell flour, < 250 μ m	15.00
2-bromo-2-nitropropane-1,3-diol	0.03
perfume	0.20
	100.00

Other surfactants, such as sodium fatty alcohol ether sulfate, cocamidopropyl betaine, or alkyl polyglycosides, or admixtures thereof may also be used for formulating the hand cleaning pastes.

The products are manufactured according to the usual and known processes which are commonly known for formulations of surfactant systems (G. Ziolkowski, Kosmetik-Jahrbuch 1986, 1987, 1989, Verlag für Chemische Industrie, H. Ziolkowski KG Augsburg; W. Umbach, Kosmetik, 1988, Georg-Thieme-Verlag Stuttgart, in particular chapters 5 and 13).

Example 7

Formulation of an anhydrous skin cleansing agent.

Raw material	Amount used/ %-wt.
fatty alcohol C ₁₂ -C ₁₈ 5 EO (washing active substances)	15.0
dimethyl adipate (solvent)	9.3
dimethyl glutarate (solvent)	35.3
dimethyl succinate (solvent)	9.4
isooctyl stearate (re-greasing agent)	5.0
fumed silica (thickener)	2.3
ethyleneglycol distearate (thickener)	7.0
cellulose acetate butyrate (thickener)	3.8
perfume	0.4
walnut shell flour, < 250 μ m, bleached	12.5
	100.0

Example 8

Formulation of a peeling cream.

A. MIGLYOL ^R 812 neutral oil (mixed acidic triglyceride of fract. C8-10 coconut fatty acids; manufacturer: Dynamit Nobel AG)	66.45%
IMWITOR ^R 780 K (manuf.: Dynamit Nobel AG)	5.0%
Teginacid ^R (mixture of glycerol mono-distearates with portions of polyglycol fatty alcohol ethers; manufacturer: TH.Goldschmidt AG)	3.4%
Texapon ^R L 100 (sodium lauryl sulfate manufacturer: Henkel KG aA)	1.45%

	paraffinic oil	2.5%
	phenonip	1.0%
	(phenoxyethanol with parabenes, Nipa Laboratories, GB)	
B.	potato starch	5.0%
	olive kernel flour < 300 μ m, bleached	6.0%
C.	Aerosil ^R 200 (pyrolytically manufactured highly disperse silicon dioxide, manufacturer: Degussa AG)	4.0%
	Syloid ^R 244 (highly disperse silicic acid; manufacturer: Grace and Co.)	6.0%
	perfume oil	0.2%
		100.00%

Example 9

Preservative test with a formulation of a solventless hand cleaning paste.

Raw material	Amount used/ %-wt.
surfactant combination consisting of Na-lauryl ether sulfate, cocamido- propyl betaine and castor oil sulfonate, (40%)	57.9
bleached or unbleached mixture of walnut shells and olive kernel flour, 50 : 50, < 300 μ m	15.0
thickener combination of carboxymethylcellulose and bentonite	5.0
titanium dioxide	0.5

citric acid		0.2
perfume		0.2
preservative acc. to Table		
water	ad	100.0

Table

concentration of the preservative (Bronopol 2-bromo-2-nitropropane- 1,3-diol)	0.00%	0.03%	0.08%
germs/g when the un- bleached mixture was used (after 2 days)	13,000 (growth)	2,400 (growth)	200 (growth)
germs/g when the bleached mixture was used (after 2 days)	< 100	< 100	< 100

When the unbleached shell/kernel-flour-mixture was used in a solventless hand cleaning paste without preservative according to the formulation of Example 9, bacterial counts of 1.3×10^4 /g were found in the product after 2 days, whereas the product did not exhibit an increased bacterial count when the bleached flour had been used.



CLAIMS

1. An abrasive for cosmetic preparations, in particular skin cleaning agents, which optionally comprise surfactants, soaps or other emulsifiers, organic solvents or oils and, optionally, thickeners, builders, re-greasing agents, perfumes, preservatives, dyes and antioxidants, characterized in that it comprises bleached natural shell and/or kernel flour.
2. The abrasive according to claim 1 characterized in that said shell and/or kernel flour has a defined particle size.
3. The abrasive according to claims 1 and 2 characterized in that it consists of finely divided shell and/or kernel flour bleached with aqueous hydrogen peroxide.
4. The abrasive according to claims 1 to 3 characterized in that the particle size amounts to 50 - 2000 μm , preferably 70 - 1000 μm , and most preferably to 80 to 400 μm .
5. The abrasive according to claims 1 to 4 characterized in that the flour of walnut shells, almond shells and hazelnut shells, that of olive kernels, apricot and cherry stones, or any mixtures of said shell and stone flours is used as said natural shell or kernel flours.
6. The abrasive according to claims 1 to 5 characterized in that it is used in anhydrous or hydrous skin cleaning agents.
7. The abrasive according to claims 1 to 6 characterized in that it comprises a content of bleached, finely divided, natural shell and/or kernel flours amounting to 3 - 95%-wt., preferably 5 - 70%-wt., and most preferably 7 - 50%-wt., relative to the total weight of the skin cleansing agent.



8. The abrasive according to claims 1 to 7 characterized in that shell and/or kernel flour is used having a particle size of 50 - 2000 μm , preferably 70 - 1000 μm , and most preferably of 80 - 400 μm .

9. A process for the production of the abrasive as defined in claims 1 to 8 characterized in that natural shells and/or kernels are ground into a flour having a defined particle size, that the flour is treated with a bleaching agent in aqueous suspension, is subsequently filtered off, washed with water and dried.

10. The process according to claim 9 characterized in that said finely divided shell and/or kernel flour is treated with aqueous hydrogen peroxide as bleaching agent.

11. The process according to claim 9 or 10 characterized in that said bleaching agent additionally comprises a stabilizer.

12. The process for the manufacture of an abrasive according to claims 9, 10, or 11 characterized in that shell and/or kernel flour is used which is ground to a particle size of 50 - 2000 μm , preferably 70 - 1000 μm , and most preferably 80 - 400 μm .

13. The process for the production of an abrasive according to claims 9 to 12 characterized in that said treatment with hydrogen peroxide is effected at a temperature of 20°C to 100°C, preferably 50°C to 100°C, and most preferably at 20°C to 50°C.

14. The process for the production of an abrasive according to claims 9 to 13 characterized in that said treatment with hydrogen peroxide is effected during a residence time of 300 to 30 minutes, preferably of 60 to 30 minutes.



15. The process for the production of an abrasive according to claims 9 to 14 characterized in that said hydrogen peroxide in said aqueous suspension has a concentration of 1.0 to 10.0% by weight, preferably of 1.0 to 3.0% by weight.

16. The process for the production of an abrasive according to claims 9 to 15 characterized in that the bleached and washed material is dried at 100°C to 170°C, preferably at 120°C to 150°C, more preferably under vacuum within a temperature range of 60°C to 140°C.

17. The process for the production of an abrasive according to claims 9 to 16 characterized in that drying is effected up to a residual moisture content of 10.0%-wt., preferably of 0 to 8.0%-wt.

18. The use of the abrasive as defined in claims 1 to 8 in anhydrous or hydrous skin cleansing agents comprising surfactants, soaps or other emulsifiers, organic solvents or oils, as well as, optionally, thickeners, builders, dyestuffs, and antioxidants, characterized by a content of bleached, disperse, natural shell and/or kernel flour as abrasive to support skin cleaning.

19. The use of the abrasive according to claim 18 in skin cleansing agents characterized in that the flour of walnut shells, hazelnut shells or almond shells, or that of olive kernels, apricot or cherry stones, or any mixtures thereof, is used as said natural shell and/or kernel flour.

20. The use of the abrasive according to claims 18 and 19 in skin cleaning agents characterized by a content of bleached, finely divided, natural shell and/or kernel flours amounting to 3 - 95%-wt.,



preferably 5 - 70%-wt., and most preferably 7 - 50%-wt., relative to the total weight.

21. The use of the abrasive according to claims 18 to 20 in hand cleaning pastes.

22. Cosmetic preparations, in particular hand detergents and hand cleaning agents, comprising an abrasive according to claims 1 to 8 or one manufactured according to claims 9 to 17.