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(54) **Coated detergent drawer**

(57) Washing machine, both top or front loader, comprising a washing aid dispenser (1) and a washing tub adapted to be supplied, through said dispenser, with a mixture of water and said washing aid. Said dispenser is provided with at least one compartment adapted to contain said washing aids, wherein at least one of said compartments is coated with or made of an anti-stick material/

layer.

Preferably said anti-stick layer is implemented by a carbon-film made of thin-film amorphous carbon.

In the best embodiment said compartments are exclusively or substantially made of plastic material, and the coating process is that one called "Plasma assisted CVD".

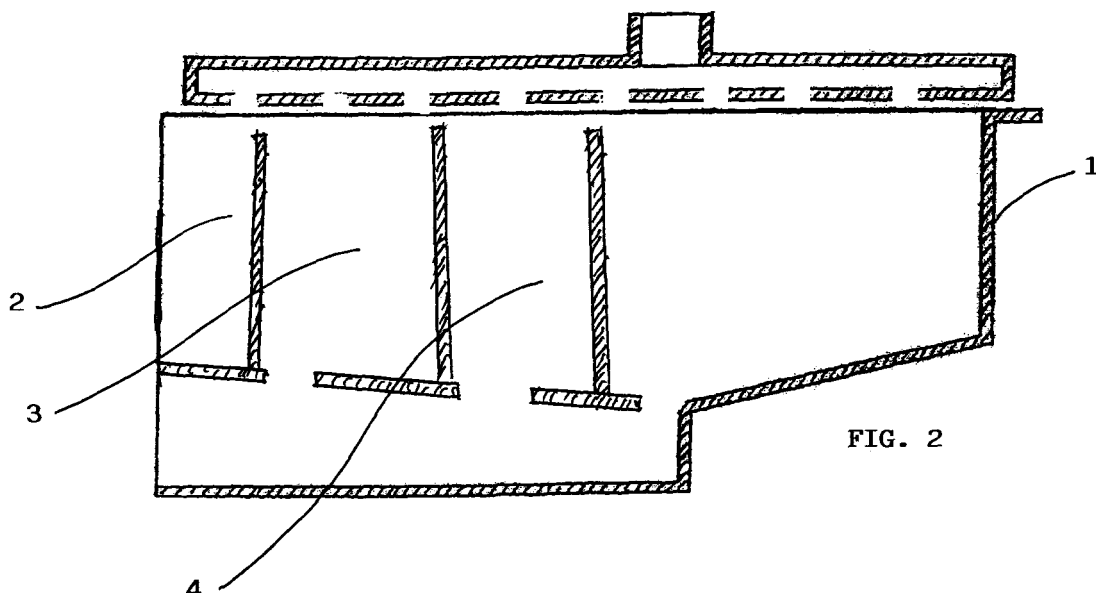


FIG. 2

Description

[0001] The present invention relates to a washing machine comprising a detergent dispenser connected to a water inlet valve means, the dispenser comprising a plurality of compartments connected to a rotating drum being accommodated in a tub, said machine being adapted to carry out successive operation phases under the control of a programme sequence control unit that is adapted to also control the water inlet valve means causing an amount of water to flow into the compartment so as to flush out the detergent contained therein and convey it into the tub.

[0002] The invention can be applied to any type of detergent dispenser, having both an extractable drawer and a front not-extractable drawer, as represented for instance in fig. 1B of EP 0 599 110 B1; moreover this invention can be used also with detergent dispensers associated to any type of top loader washing machine; however in said case the detergent dispensers are very diversified both in their shape and respective positioning, and therefore for sake of simplicity said type of detergent dispensers will not further discussed.

[0003] Therefore, even if in the following a detergent dispenser will be shown which is typically of the type intended to be used with an extractable drawer in a front loader washing machine, it is here clearly understood that the invention core is typically applicable to any type of detergent drawer, however formed or arranged.

[0004] Current domestic automatic washing machines usually comprise a tub adapted to hold inside the rotating drum accommodated therein the clothes that can be treated with water in which, in respective operational phases of the washing process, various laundering aids are diluted. Such laundering aids are let into the tub of the machine through the detergent dispenser, which can for example be of the pull-out drawer type, comprising adjacent and separate compartments, e.g. three such compartments for holding the prewash detergent, the main wash detergent and the rinsing aid or fabric softener, respectively, in which respective amounts of various such laundering aids can be filled, according to the selected operation cycle of the machine.

[0005] Mostly this dispenser is placed so that it is accessible by the user and in convenient position for filling with detergent. Its location can be at the top of the machine, above water level in the tub. The washing aid is flushed in by fresh water at the beginning of the appropriate cycle. The duration of the fresh water is controlled by the programme sequence control unit and restricted by the amount of water that is used in the respective programmes steps. However, detergent forms that do not dissolve sufficiently fast or for some reasons are not completely flushed out of the drawer can create problems.

[0006] The detergent dispenser, in particular a dispenser of the pull-out drawer type is usually shaped in a way to facilitate transport of detergent into the tub by the tap water flow. Although machine manufacturers direct large efforts on the design of detergent dispensers and the way detergents are flushed in, experience shows that detergent residues can remain anyway inside the dispenser and can accumulate and further act as breeding ground for microbial colonisation and fungal growth. The removal and manual cleaning of the pull out drawer is regarded as severe nuisance by customers.

[0007] From WO 2004/099308 A1 it is divulged a type of washing machine provided with parts manufactured with anti-microbial plastic composition; however said composition is incorporated in the whole parts bodies, and thus it cannot prevent surface sticking and colonization, due to the remaining of washing-aids residues on the bottom of the drawer compartments.

[0008] It is therefore an objective of the present invention to provide for a washing machine comprising a detergent dispenser, which does not require manual cleaning of the drawer or at least much lesser so than conventional current drawers.

[0009] According to the present invention this object is achieved in the above defined washing machine in that the detergent dispenser is coated or made from a material with very limited tendency to hold back any detergent residues, i.e. a non-stick material or coating. The features of this invention are reached through a special type of detergent dispenser incorporating the characteristic as recited in the appended claims as described below by mere way of non limiting example with reference to the accompanying drawings, in which:

fig. 1 shows a front loader washing machine provided with a detergent dispenser on which the invention can be applied,

fig. 2 shows a vertical intermediate plane section of a compartment for holding and releasing of washing aid substances,

fig. 3 shows an outer perspective view of a typical detergent drawer and of their respective inner compartments, which can be mounted in a front loader washing machine, and have to be filled with the washing aid substances from above.

[0010] With ref. to the figures, the detergent dispenser 1 comprises a plurality of compartments 3, 4, 5, opened upwards, into which the product, to be flushed into the washing tub, is poured.

On the bottom of said compartments some residual parts of said products are formed; said residues have to be removed.

[0011] It is well known that such removing action is carried out by a water flush which draws them into the tub; however

a part of such substances remains stuck on the bottom of the respective compartment, and this fact generates the problem the instant patent aims to solve.

[0012] After systematic tests and evaluations, it was observed that the prevention /removal of such residual products is especially favoured if the walls compartments are treated, on their relevant surfaces, with a Carbon-like coating, consisting in the deposition of a single- or multi-layered film of Diamond-like coating, or DLC, as it is usually known in the field of the technique.

[0013] Such kind of treatment, when applied on general surfaces, and the relevant used substances are widely known in the art; however, for the reader's convenience, the Annex "A" to the instant document shows a scientific text relevant to the nature, to the features and to the various coating technologies for the production of Diamond-like carbon films, which is anyway known and available in the scientific documentation.

[0014] In order to improve the overall economic effectiveness of such process, it is also advisable that it be carried out using really convenient methods which could be easily implemented on mass production, even if a first-class quality is not strongly requested.

[0015] To this purpose a process known as "PLASMA ASSISTED CVD", whose features are better specified in the attached Annex "A"; said process has to be implemented at temperatures compatible with the support material of said compartments, and to this purpose said detergent dispenser is preferably made of thermo-plastic substances.

[0016] Moreover it was also experienced that an optimum compromise between:

the thickness of coating obtained with one of said methods, on which obviously the desired advantages are depending, and the respective costs, is achieved when the coating thickness is comprised between 1 nm and 5 micron, preferably obtained through only one coating, even if obviously said coating may be a single or a multi-layered film.

ANNEX "A"

http://en.wikipedia.org/wiki/Diamond-like_carbon

[0017] Diamond-like carbon (DLC) is an umbrella term that refers to 7 forms[1] of amorphous carbon materials that display some of the unique properties of natural diamond.

[0018] They are usually applied as coatings to other materials that could benefit from some of those properties. All seven contain significant amounts of sp³ hybridized carbon atoms. The reason that there are different types is that even natural diamond can be found in two crystalline polytypes. The usual one has its carbon atoms arranged in a cubic lattice, while the very rare one (lonsdaleite) has a hexagonal lattice. By mixing these polytypes in various ways at the nanoscale level of structure, DLC coatings can be made that at the same time are amorphous, flexible, and yet purely sp³ bonded "diamond". The hardest, strongest, and slickest is such a mixture, known as tetrahedral amorphous carbon, or ta-C. For example a coating of only 2µm thickness of ta-C increases the resistance of common (ie. type 304) stainless steel against abrasive wear; changing its lifetime in such service from one week to 85 years. Such ta-C can be considered to be the "pure" form of DLC, since it consists only of sp³ bonded carbon atoms. Fillers such as hydrogen, graphitic sp² carbon, and metals are used in the other 6 forms to reduce production expenses, but at the cost of decreasing the service lifetimes of the articles being coated. The various forms of DLC can be applied to almost any material that is compatible with a vacuum environment. In 2006, the market for outsourced DLC coatings was estimated to be about 30,000,000 € in the EU.

[0019] DLC is typically produced by processes in which high energy precursive carbons (eg. in plasmas, in sputter deposition and in ion beam deposition) are rapidly cooled or quenched on relatively cold surfaces. In those cases cubic and hexagonal lattices can be randomly intermixed, layer by atomic layer, because there is no time available for one of the crystalline geometries to grow at the expense of the other before the atoms are "frozen" in place in the material. Amorphous DLC coatings can result that have no long range crystalline order. Without long range order there are no brittle fracture planes, so such coatings are flexible and conformal to the underlying shape being coated, while still being as hard as diamond.

[0020] There are several methods for producing DLC, but all depend upon the fact that in carbon the sp³ bond length is significantly less than the length of the sp² bond. So the application of pressure, impact, catalysis, or some combination of these at the atomic scale can force sp² bonded carbon atoms closer together into sp³ bonds. This must be done vigorously enough that the atoms cannot simply spring back apart into separations characteristic of sp² bonds. Usually techniques either combine such a compression with a push of the new cluster of sp³ bonded carbon deeper into the coating so that there is no room for expansion back to separations needed for sp² bonding; or the new cluster is buried by the arrival of new carbon destined for the next cycle of impacts. It is reasonable to envision the process as a "hail" of projectiles that produce localized, faster, nanoscale versions of the classic combinations of heat and pressure that produce natural and synthetic diamond. Because they occur independently at many places across the surface of a growing film or coating, they tend to produce an analog of a cobblestone street with the cobbles being nodules or clusters

of sp^3 bonded carbon. Depending upon the particular "recipe" being used, there are cycles of deposition of carbon and impact or continuous proportions of new carbon arriving and projectiles conveying the impacts needed to force the formation of the sp^3 bonds. As a result, ta-C may have the structure of a cobblestone street, or the nodules may "melt together" to make something more like a sponge or the cobbles may be so small as to be nearly invisible to imaging. A classic "medium" morphology for a ta-C film is shown in the figure.

[0021] Diamond like coatings or diamond like carbon are terms used for thin coating made up of carbon in varying degree of crystallization and bonding by sp^2 or sp^3 bonds.

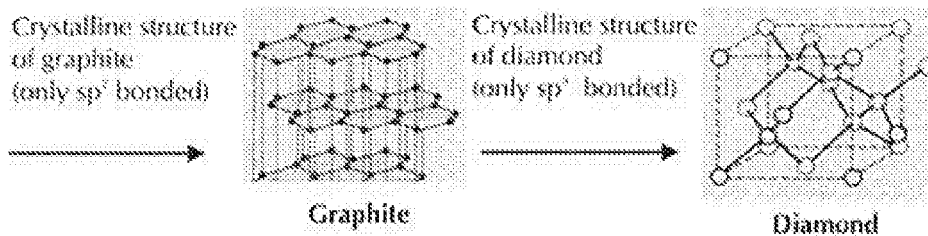
Coating Definitions

[0022] Diamond-like Coatings are amorphous carbon based coatings with a high hardness and a low coefficient of friction. Their unique composition and structure results in excellent wear resistance and non-sticking characteristics. These coatings are thin, chemically inert and have a low surface roughness. They can be tailored to have a wide range of electrical resistivity.

[0023] The standard thickness of these layers is situated between 0,002 and 0,004 mm.

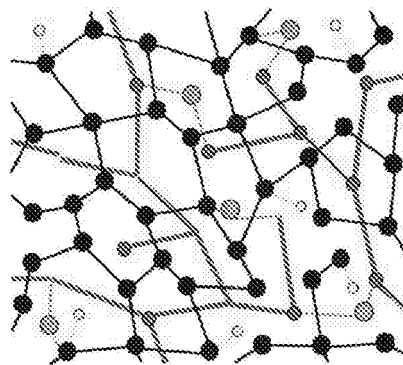
Diamond-like carbon coatings (a-C:H)

[0024] DLC coatings are a mixture of sp^2 and sp^3 bonded carbon atoms with a hydrogen concentration between 0 - 80%.



[0025] This coating provides the highest hardness and abrasion resistance characteristics.

[0026] Typical applications include high wear environments involving molds and metal forming.



Typical
Composition

[0027] Diamond-like nanocomposite coatings (a-C:H/a-Si:O; DLN)

[0028] This coating exhibits the lowest coefficient of friction, even in high humidity or wet environments. It offers the best possible combination of anti-stick and wear behaviour.

[0029] Typical applications include printer-copier equipment, insert cores and many others.

[0030] These coatings comprises C, H, Si and O:

a-Si:O-> enhances high temperature stability, leads to lower friction & lowers films stress

a-C:H-> diamond-like properties

Metal-doped Dylyn (Me/a-C:H/a-Si:O; DLN)

[0031] The electrical characteristics of the coatings can be tailored by the addition of metal dopants. This creates an engineered surface for specialized applications requiring a combination of wear, low friction and electrical conductivity. Typical applications include those requiring static discharge in addition to wear resistance, such as watermanufacturing.

Coating technology

[0032] Diamond-Like Carbon and Diamond-Like Nanocomposite coatings are deposited using a PACVD (plasma-assisted chemical vapor deposition) process, at deposition temperatures below 200°C (400°F). Using this technology, both electrically conductive and non-conductive substrates in a variety of shapes and sizes can be coated homogeneously.

This environmentally friendly technology can be scaled up.

[0033] Another deposition technology is also used: Physical Vapor Deposition. PVD refers to depositing atoms on one surface by physically removing them from another surface. It allows the design of advanced (or engineered) interlayers to improve the performance of the coating in specific applications.

[0034] Unlike crystalline diamond coatings, which require high temperatures to deposit and have very rough surfaces, the stress-free coatings are deposited at room temperature and are extremely smooth. Furthermore, these stress-free coatings are almost identically as hard as the crystalline films. These coatings are also much more stable than amorphous diamond films that contain hydrogen - industry's most common hard carbon coating. "Diamond coatings that contain hydrogen tend to degrade at temperatures as low as 200 degrees Celsius. The stress-free coatings show negligible degradation up to 800 degrees Celsius." The process uses a pulsed laser on a graphite target to deposit, at room temperature, an amorphous carbon film with a high percentage of diamond-like bonds but with high initial stress.

[0035] When the deposited material is heated these films lose their stress, yet retain their diamond-like properties. In contrast, amorphous diamond films that contain hydrogen convert to graphite upon heating.

[0036] The stress relaxation that occurs in the stress-free coatings is uniquely different from other types of stress relaxation we have seen in the past.- The process seems to involve short-range bond rearrangement as opposed to long-range atomic migration, which occurs in many other materials.

http://www.sandia.gov/LabNews/LN04-10-98/diamond_story.html

Guideline VDI 2840: Carbon coatings - Basic knowledge, coating types and properties 12.10.2005

[0037] In order to give all laymen clarity with the existing multiplicity from confusing terms and trade names, the guideline contains a unique classification and nomenclature, in particular for diamond-like-carbon (DLC) and diamond films. On the other hand the potential user can pre-select suitable carbon film types for coated work pieces and tools. A characterizing section recalls the important characteristics of the individual film types, which are manufactured industrially today.

Methods for Producing DLC Films

Several methods have been developed for producing diamond-like carbon films:

primary ion beam deposition of carbon ions (IBD)

sputter deposition of carbon with or without bombardment by an intense flux of ions (physical vapour deposition or PVD)

deposition from an RF plasma, sustained in hydrocarbon gases, onto substrates negatively biased (plasma assisted chemical vapour deposition or PACVD). Plasma Assisted CVD

[0038] Plasma assisted CVD techniques employing RF and DC glow discharges in hydrocarbon gas mixtures produce smooth amorphous carbon and hydrocarbon films, which have mixed sp² and sp³ bonds. These exhibit hardness values of 900-3000Hv. The CVD processes will generally require deposition temperatures of at least 600°C to give the required combination of properties, however, low temperature deposition is possible. The CVD technique gives good deposition rates and very uniform coatings, and is suited to very large-scale production.

Ion Beam Deposition

[0039] Another technique for DLC deposition is based on ion beam deposition. This has the advantage of being able to deposit high quality coatings at very low temperatures (near room temperature). The disadvantages are that the deposition rate is very low (1µm/hr maximum) and that even substrates of simple geometry need complex manipulation to ensure uniform deposition.

[0040] The Closed Field Unbalanced Magnetron Sputter Ion Plating Process

A technique has now been developed that can readily apply a-C:H films ($>4\mu\text{m}$) to substrates of any shape. The process is based on closed field unbalanced magnetron sputter ion plating (CFUBMS), figure 1, combined with plasma assisted chemical vapour deposition. The commercial importance of such a development is already being seen and the potential range of applications and possibilities are enormous. The technique is highly innovative and it provides the flexibility required to ensure excellent adhesion to any substrate, and the coating of any component shape or material, in a high productivity industrial process.

[0041] The new technique combines the benefits of both plasma CVD and ion beam deposition. The deposition is carried out at 200°C in a closed field unbalanced magnetron sputter ion plating system (Teer Coatings UDP 400 or 800 series). The system was originally designed for reactive deposition of metal nitrides, carbides and oxides. The inherent versatility of the process has enabled the deposition of DLC in the system by combining two established techniques, PVD and CVD. Low pressure RF plasma CVD is adopted for high rate deposition ($>5\mu\text{m/hr}$), in combination with simultaneous ion assistance and physical vapour deposition from unbalanced magnetron sputtering sources, to give very high quality films. As with beam techniques, the low pressure of the process means that deposition is to some extent line-of-sight, which means that substrate manipulation is necessary to ensure uniform deposition. However, because the substrates are surrounded by four long magnetrons ($>1\text{m}$ in length if necessary) the coating flux impinges on the substrates from all directions and, usually, only simple single axis rotation during deposition is necessary. Deposition of Stress-Free Films

[0042] One of the main problems with DLC deposition at low temperature, is the creation of very high internal stress levels in the films. This, combined with the ensuing lattice mismatch when DLC is applied to a wide range of substrates, commonly leads to poor adhesion. In high mechanical stress applications, the adhesion of the films is of paramount importance. This problem has now been overcome by ensuring that there are no stress concentrations near the coating/substrate interface. The magnetron sources are used to reactively deposit a series of multilayer compounds prior to deposition of the DLC. The layers have graded interfaces. This ensures that there are no abrupt changes in composition, and that the stress is introduced into the film gradually. The optimum multilayer structure series is: titanium, titanium nitride, titanium carbonitride, titanium carbide, and then the DLC. It has also been subsequently found that the mechanical properties of the hard carbon films can be improved by incorporating a small percentage of metal dopant (usually $\sim 5\%$ titanium) in the final carbon structure.

[0043] The resulting films have excellent friction and wear properties.

http://www.diamondcoating.net/Types_of_hard_carbon.htm

[0044] Types of Diamond like carbon (DLC) Diamond-like carbon (DLC) is an umbrella term that refers to 7 forms of amorphous carbon materials that display some of the unique properties of natural diamond. The German Fraunhofer - IST institute has organized them into the chart form seen in this page background.

[0045] In 2006 the Association of German Engineers, VDI, the largest engineering association in Western Europe issued an authoritative report VDI_2840 in order to clarify the existing multiplicity of confusing terms and trade names. It provides a unique classification and nomenclature for diamond-like-carbon (DLC) and diamond films. It succeeded in reporting all information necessary to identify and to compare different DLC carbon films that are shown in the Fraunhofer-IST chart and which are offered on the market.

[0046] The hardest, strongest, and slickest DLC is known as tetrahedral amorphous carbon, or ta-C. Such ta-C can be considered to be the "pure" form of DLC, since it consists only of sp^3 bonded carbon atoms. Fillers such as hydrogen, graphitic sp^2 carbon, and metals are used in the other 6 forms to reduce production expenses, but at the cost of decreasing the service lifetimes of the articles being coated.

[0047] The authoritative German VDI 2840 standards report affirms the superiority of ta-C.

[0048] These $[\text{sp}^3]$ bonds can occur not only with crystals - in other words, in solids with long-range order - but also in amorphous solids where the atoms are in a random arrangement. In this case there will be bonding only between a few individual atoms and not in a long-range order extending over a large number of atoms. The bond types have a considerable influence on the material properties of amorphous carbon films. If the sp^2 type is predominant the film will be softer, if the sp^3 type is predominant the film will be harder.

[0049] A secondary determinant of quality was found to be the fractional content of hydrogen. Some of the production methods involve hydrogen or methane as a catalyst and a considerable percentage of hydrogen can remain in the finished DLC material. When it is recalled that the soft plastic, polyethylene is made from carbon that is bonded purely by the diamond-like sp^3 bonds, but also includes chemically bonded hydrogen, it is not surprising to learn that fractions of hydrogen remaining in DLC films degrade them almost as much as do residues of sp^2 bonded carbon.

[0050] To identify which of the forms is on a particular sample, the fraction of hydrogen and the fraction of sp^3 bonded carbon atoms (not graphite) must be measured. Knowing those two numbers enables a user to plot the "location" of the sample on the VDI-map. The closer to the upper left corner that a material plots, the better (and more) pure is the DLC. Dilutions with hydrogen and graphitic carbon degrade the DLC.

Claims

1. Washing machine, both top or-front loader, comprising a washing aid dispenser (1) and a washing tub adapted to be supplied, through said dispenser, with a mixture of water and said washing aids, said washing aid dispenser being provided with at least one compartment (3, 4, 5) which is adapted to contain said washing aids, **characterized in that** at least one of said compartments (3, 4, 5) of said dispenser is coated with or made of an anti-stick material / layer.
2. Washing machine according to claims 1 or 2, **characterized in that** said anti-stick layer is implemented by a carbon-film.
3. Washing machine according to claims 1 or 2, **characterized in that** said carbon-film is made of thin-film amorphous carbon.
4. Washing machine according to claim 3, **characterized in that** said compartments are exclusively or substantially made of plastic material, and that the coating process is that one called "Plasma assisted CVD".
5. Washing machine according to any of the previous claims, **characterized in that** said anti-stick layer is applied on the inner surface only of said compartments.
6. Washing machine according to claim 3 on, **characterized in that** said the thickness of said thin diamond like carbon layer is comprised between 1 nm and 5 μ m.

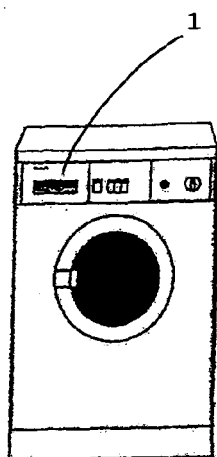


FIG. 1

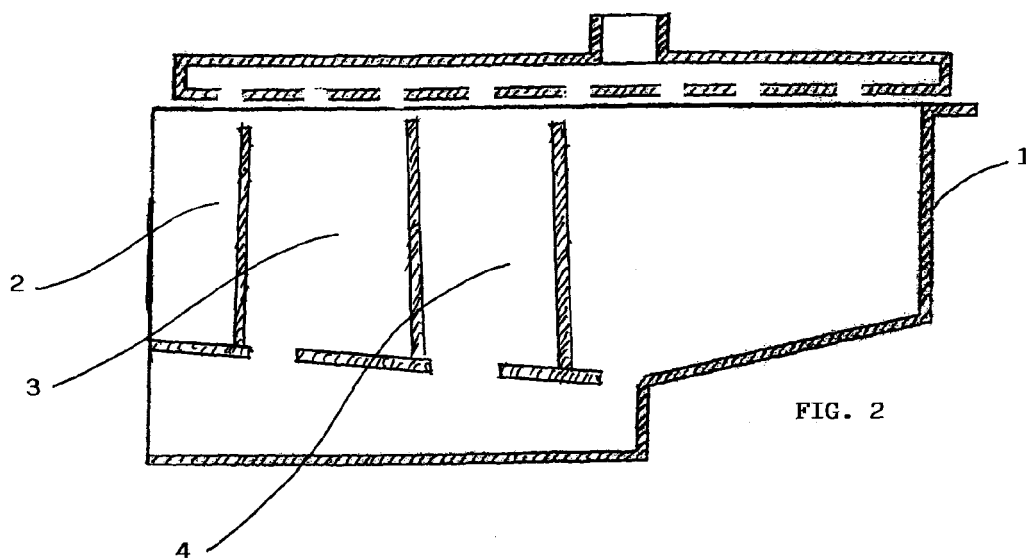


FIG. 2

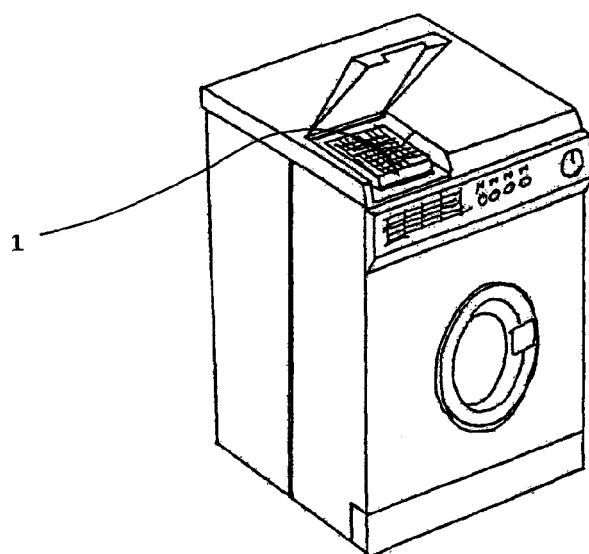


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 11 0928

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 101 22 514 A1 (AEG HAUSGERAETE GMBH [DE]) 14 March 2002 (2002-03-14)	1	INV. D06F39/02
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		30 October 2007	Jeziński, Krzysztof
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			

3
EPO FORM 1503 03.82 (P04C01)

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

EP 07 11 0928

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
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30-10-2007

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