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(54) **Non-pneumatically assisted spray-coating of a surface with viscous aqueous architectural coating composition**

(57) A process, apparatus and coating composition for the non-pneumatically assisted (eg airless) spray-coating of a surface with a viscous aqueous architectural coating composition (eg. a paint) suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and contains a binder polymer and over 30wt% of solid ingredients (especially those chosen from thickeners, opacifiers, pigments and extenders) in which the composition is expelled from an orifice in a nozzle

under a pressure of 2.5 to 5bar generateable by hand-pump. A suitable composition has a Brookfield viscosity of at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec. and contains a predominantly associative thickener for spraying through an oblate or circular orifice or alternatively has an apparent extensional viscosity of from 0.05 to 0.5Pa.sec. Preferably, the nozzle has means to impart a transverse force to the composition so that it enters the orifice with a swirling motion.

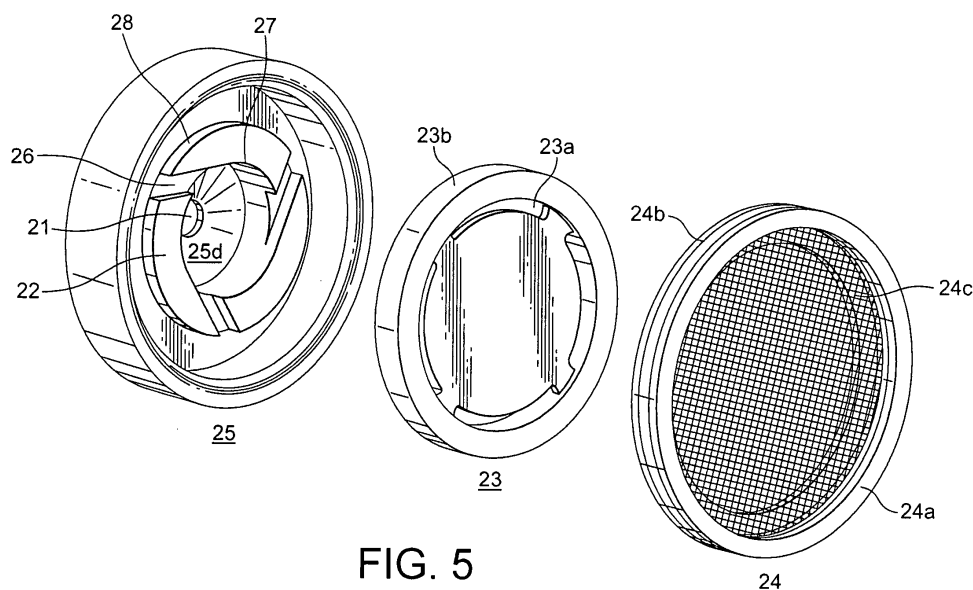


FIG. 5

Description

[0001] This invention relates to a process and apparatus for the non-pneumatically assisted spray-coating of a surface with a viscous aqueous architectural coating composition being a composition suitable for hiding marks on surfaces which process is able to cope with non-Newtonian flow using pressures of no more than 5 bar. In practice, "non-pneumatically assisted spray-coating" usually means that the formation of the spray is not assisted by the injection of air but occasionally other gases such as carbon dioxide are used instead of air and so for brevity, "airless" will be used in this description to denote spray-coating in which spray formation is unassisted by air or by any other gas. The invention also relates to a coating composition for use in the process and apparatus.

[0002] The significance of pressures of up to 5 bar is that these are pressures achievable from simple hand-operated compressors, usually known less precisely as "hand-pumps".

[0003] Architectural coating compositions are nearly always paints and so for brevity, "paints" will frequently be used in this description to denote architectural coating compositions in general. Most paints suitable for hiding marks exhibit non-Newtonian flow resulting from their pseudoplastic nature which causes them to undergo non-linear reductions in viscosity when subjected to high shear. Despite over 70 years of spray painting (albeit at high pressures), there is still no simple or reliable way of predicting how such non-linear reductions in viscosity will affect the characteristics of the sprays obtained.

[0004] Architectural paints are designed for application to surfaces found in or as part of buildings such as walls, ceilings, window frames, doors and door frames, radiators and customised furniture. Some paints are particularly designed for application to external surfaces of buildings and to surfaces found on land (eg. gardens and yards) surrounding buildings. Such surfaces are usually stone, brick or concrete and the paints are expected to be reasonably able to hide marks on the surfaces. The paints are intended to be applied on site at ambient temperatures and humidities by either amateur or professional painters. European ambient temperatures met during painting on site are typically from 5 to 45°C. For paints to be reasonably suitable for hiding marks, they should contain sufficient opacifiers, pigments and/or extenders to give the paint a total solids content of at least 30wt% (based on the total weight of the paint before drying) and preferably a solids content of from 40 to 70wt% with 43 to 55wt% being the most preferred range. "Extenders" are solid particles of for example clays and/or chalk which are added to architectural coating compositions in order to space apart pigment and/or opacifier particles whereupon they increase their pigmentation and opacifying efficiencies. A fuller description of them is given in the third edition of an "Introduction to Paint Chemistry" by G P A Turner, published in 1967 by Chapman and Hall of London, the contents of which are herein incorporated by reference.

[0005] Application may be by brush or roller or, if the painters are professionals, by (optionally air-assisted) sprays generated using pressures of over 130 bar. The spray painting of large areas is of the order of five to ten times faster than painting by brush, but the high pressure apparatus used is both too expensive and too hazardous for use by amateur, ie "Do-it-Yourself" painters.

[0006] Inexpensive low pressure spraying apparatus which can be pressurised up to about 3 bar using a hand-pump is widely used by amateurs (especially gardeners) for spraying organic solvent-based liquids such as woodstains, fungicides and insecticides which contain low or zero contents of solid material and have negligible Brookfield viscosities which means that they exhibit Newtonian flow making them easy to spray. Attempts to use such apparatus to spray aqueous paints having a Brookfield viscosity at 22° C of over 0.5 Pa.sec and solids contents above 7 wt % have resulted in the production of approximately cylindrical jets of small radii which impact onto no more than a tiny and approximately circular area of a target surface. The small size of this area would make the painting process very time consuming.

[0007] The brochure "Cuprinol introducing a major breakthrough in Fence Treatments for 2005" published in 2005 describes commercially available apparatus for spraying non-Newtonian architectural coating compositions using pressures of up to 5 bar generated by a hand-pump. The architectural coating composition is contained in a reservoir which is pressurised by the pump to deliver the composition through a nozzle to an elongated slot formed in the nozzle from which slot the composition issues as a fan-shaped flat spray. However, it has been discovered that the apparatus can only be used successfully with architectural coating compositions having solid contents of below about 12wt% for otherwise, the architectural coating composition either fails to emerge from the slot or it does not emerge as a useable spray or jet. One possible reason for failure when the solids content is high is that too much of the energy in the flow of paint entering the nozzle is consumed in shearing the flow adjacent the walls of the slot and in causing particles of solids in the paint to rotate. Before explaining how this problem can be overcome, it will be helpful to describe a little of the formulation of aqueous architectural paints and of the way in which they acquire their viscosity.

[0008] Aqueous architectural paints typically comprise an aqueous latex of organic film-forming binder polymer which serves firstly to bind a dried coat of the composition to a surface to which it has been applied and secondly to bind any other ingredients of the composition such as pigments, dyes, opacifiers, extenders and biocides into the dried coat. The binder polymer is a significant cause of non-Newtonian flow.

[0009] A wide variety of conventional film-forming binder polymers are available for use in aqueous architectural paints, but those most commonly used are of three broad types obtained from ethylenically unsaturated monomers and they

are known colloquially as "acrylics", "vinyls" or "styrenics". The "acrylics" are usually copolymers of at least two alkyl esters of mono-ethylenically unsaturated carboxylic acids (eg. methyl, ethyl, butyl or 2-ethylhexyl esters of acrylic or methacrylic acids such as methyl methacrylate/butyl acrylate copolymer) optionally with some non-esterified acid (eg. acrylic or methacrylic acid). "Vinyls" usually comprise copolymers of a mono-vinyl ester of a saturated carboxylic acid such as vinyl acetate and at least one of either an acrylic monomer or a different mono-vinyl ester, for example the vinyl ester of a carboxylic acid containing 10 to 12 carbon atoms such as those sold under the trade name "Versatate" by Resolution Europe BV of Rotterdam. The "styrenics" are copolymers containing styrene (or a similar mono-vinyl aromatic monomer) together with a copolymerisable monomer which is usually an alkyl ester of acrylic or methacrylic acid. A fuller description of suitable aqueous binder polymers is given in Turner, *ibid*.

[0010] Architectural paints need to have a viscosity at low shear (ie. a Brookfield viscosity at 22°C) of at least 0.5 Pa.sec (Pascal.second) so that if they are applied to a vertical surface in a conventional thickness in the range 0.02 to 0.05mm, the applied coating will generally resist "sagging", ie. running down the surface before the coating has had time to dry enough to lose its fluidity. "Sagging" is illustrated in Plate 14 of the "Handbook of Painting and Decorating Products" by A H Beckly published in 1983 by Granada of London, the contents of Plate 14 are herein incorporated by reference. In aqueous paints, much of the viscosity is usually imparted by the inclusion cellulosic thickeners of long or medium chain lengths and these too contribute to non-Newtonian flow. A fuller description of thickeners suitable for use in aqueous architectural coating compositions is given by E J Schaller and P R Sperry in Chapter 4 of Volume 2 of "The handbook of Coatings Additives" edited by L J Calbo, the contents of which Chapter 2 are herein incorporated by reference.

[0011] Schaller and Sperry explain that there is a need for thickeners in aqueous latex paints to adjust viscosity in order to control various properties of the paints including sagging and also film build and levelling. They list the various ways in which viscosity can be increased, but conclude that thickeners (which they alternatively call "water-soluble polymers") afford a much more efficient and controllable means of adjusting viscosity. Schaller and Sperry continue by distinguishing between two types of thickeners known as "non-associative thickeners" and "associative thickeners". Non-associative thickeners are water soluble (or at least water-swellaable) polymers which increase viscosity mainly by overlap and/or entanglement of their polymer chains and/or by their occupation of large volumes of space within the paint. These affects are promoted by the molecular weight, stiffness and straightness of their polymer chains. Associative thickeners are also water-soluble (or at least water-swellaable) polymers. They have chemically attached hydrophobic groups that are capable of self-association into micellar-like assemblies as well as being capable of non-specific adsorption onto all colloidal surfaces present. This behaviour is analogous to that of conventional surfactants. It results in a transient network of polymer chains which increase the Brookfield viscosity of paints.

[0012] By far the most important non-associative thickeners are the long, medium or short chain cellulose ethers known as "cellulosics" which comprise straight and stiff polymeric backbones making cellulosics exceptionally effective in increasing the viscosity of aqueous systems. Chain length is defined in terms of weight average molecular weights as derived from viscosity measurements. Examples of cellulosics include hydroxyethyl cellulose, sodium carboxymethyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose and ethylhydroxyethyl cellulose.

[0013] Long chain (eg. molecular weights above 250 000 Da) and medium chain (eg. 100 000 to 250 000 Da) cellulosics increase viscosity by chain entanglement which enables high Brookfield viscosities to be achieved at low concentrations. However if the concentrations of long and medium chain cellulosics have to be increased to achieve high viscosities at high shear (which is needed for high film build), they will inhibit atomisation of the coating composition during spraying resulting in excessive and uneven film build and sagging.

[0014] Short chain cellulosics (eg. molecular weights below 100 000 Da) increase viscosity mainly by concentration affects (eg. occupation of volume) and so they are less likely to inhibit atomisation during spraying. However, high concentrations are needed to achieve the required Brookfield viscosities. Such high concentrations are expensive to use and in addition, they significantly harm the water-resistance of the dried coat making it vulnerable to rain or water condensation.

[0015] Associative thickeners are relatively low in molecular weight and they overcome some of the shortcomings of cellulosics. The transient networks they create produce increases in Brookfield viscosity comparable with those achievable with high molecular weight cellulosics. This allows them to be used in relatively small concentrations which do not seriously detract from the water-resistance of the dried coating.

[0016] Schaller and Sperry report that four main types of associative thickeners have found commercial use in aqueous coating compositions. The first main type is the hydrophobically modified alkali soluble emulsion or "HASE" type. Commercial examples of HASE types have hydrophilic backbones comprising salts of polymerised or copolymerised unsaturated carboxylic acids or acid anhydrides such as acrylic or methacrylic acids or maleic anhydride. Hydrophilic moieties such as polyalkylene glycols (eg. polyethylene glycol) are attached to the hydrophilic backbones and hydrophobic groups are in turn attached to the hydrophilic moieties. In use, solutions of these HASE thickeners are added as free-flowing liquids to a coating composition at neutral or slightly acidic pH. An increase in Brookfield viscosity is then caused by raising the pH to mildly alkaline conditions (say 8 to 9) whereupon carboxylate anions are formed.

[0017] The second type of associative thickener is the hydrophobically modified hydroxy alkyl (especially ethyl) cel-

lulosic or "HMHEC" type conveniently made by the addition of long chain alkyl epoxides to hydroxyalkyl celluloses of the type used as non-associative thickeners.

[0018] The third type of associative thickener is the block/condensation copolymer "HEUR" type comprising hydrophilic blocks and hydrophobic blocks usually terminating in hydrophobic groups. The hydrophilic blocks may be provided by polyalkylene oxide (especially polyethylene oxide) moieties of relatively low molecular weight of say below 10 000Da, preferably 3 400 to 8 000Da. The hydrophilic blocks are condensed with for example hydrophobic urethane-forming diisocyanates such as toluene diisocyanate.

[0019] The fourth type of associative thickener is the hydrophobically modified polyacrylamide type in which the hydrophobic groups are incorporated as free radical copolymers with N-alkyl acrylamides. These are most useful in acidic coating compositions.

[0020] A fifth major type of associative thickener has been introduced since Schaller and Sperry's review. This is the hydrophobically modified ethoxylated oxide urethane alkali-swelling emulsion or "HEURASE" type. This type combines the functionality of the HASE and HEUR types.

[0021] It has now been discovered that where a non-Newtonian architectural coating composition has a high solids content and derives significant amounts of its viscosity from thickeners, there nevertheless exist conditions which permit useful non-pneumatically assisted spraying of the composition even when the composition is sprayed using inexpensive spraying apparatus operating at pressures low enough to be easily generated using a simple and inexpensive hand-pump, these being hand pumps which can be both afforded and used safely by an amateur.

[0022] Accordingly, this invention provides a process for the non-pneumatically assisted (eg. airless) spray-coating of a surface with a viscous aqueous architectural coating composition (eg. paint) suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and contains a binder polymer and other solid ingredients (especially those chosen from thickeners, opacifiers, pigments and extenders) and which process comprises expelling the composition under pressure from an orifice formed in a nozzle wherein:

- a) the solids content of the composition is at least 30wt% (preferably 35 to 65 wt% and most preferably 40 to 53wt%) of the total weight of the composition,
- b) the composition has a Brookfield viscosity when measured at 22°C of at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec and most preferably a Brookfield viscosity of from 1 to 12 Pa.sec,
- c) the composition contains from 0.08 to 0.6 wt% based on the total weight of the composition of thickener where over 50 wt% (based on the total weight of thickener) is associative thickener,
- d) the orifice has either an oblate circumference or preferably a circular circumference and
- e) the composition is subjected to a pressure (conveniently generated by a hand-pump) of from 2.5 to 5 bar prior to expulsion from the orifice.

[0023] It has been found that thickening by the above amounts of predominantly associative thickener gives the composition an apparent extensional viscosity which permits effective spraying even at pressures no higher than those which can be reasonably generated by a hand-pump provided that the orifice is elliptical and preferably circular. By "oblate" is meant a having a curved circumference (including an elliptical circumference) where the circumference has a longest diameter and also shorter diameters but where the shortest diameter is not less than half of the length (and preferably not less than at least four fifths of the length) of the longest diameter. Preferably, the composition should contain not more than 0.4wt% of thickener so as to minimise any loss of pouring ability and at least 0.1wt% of thickener to minimise any risk of loss sag resistance. Preferably the thickener should comprise 60 to 80 wt% (based on the total weight of thickener) of associative thickener with balance being non-associative thickener. It is possible, but expensive, to have over 80wt% and up to 100wt% of associative thickener. The most preferred concentrations of associative thickener are from 0.1 to 0.3wt% based on the total weight of the composition.

[0024] The invention alternatively provides a process for the non-pneumatically assisted (eg. airless) spray-coating of a surface with a viscous aqueous architectural coating composition (eg. paint) suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and contains a binder polymer and other solid ingredients (especially those chosen from thickeners, opacifiers, pigments and extenders) and which process comprises expelling the composition under pressure from an orifice formed in a nozzle wherein:

- a) the solids content of the composition is at least 30wt% (preferably 35 to 65 wt% and most preferably 40 to 53wt%) based on the total weight of the composition,
- b) the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec (and preferably from 0.15 to 0.35 Pa.sec) together with a Brookfield viscosity when measured at 22°C of at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec and most preferably, a Brookfield viscosity of from 1 to 12 Pa.sec and
- c) the composition is subjected to a pressure (conveniently generated by a hand-pump) of from 2.5 to 5 bar prior to expulsion from the orifice. It has been found that the selection of compositions having the above range of apparent

extensional viscosities permits effective spraying even at pressures which can be reasonably generated by a hand-pump, especially if the orifice is oblate or preferably circular.

[0025] For the purposes of this description, the apparent extensional viscosity, η_a , of a complex non-Newtonian fluid such as an aqueous architectural coating composition is defined to be

$$\eta_a = \frac{\sigma}{\frac{\delta d}{\delta t}}$$

where σ is the surface tension of the coating composition at 25°C and $\delta d/\delta t$ is the rate of decrease with respect to time, t , of the diameter, d , of a vertical capillary filament of the composition at its mid-point which capillary is formed when the composition is placed between two vertically opposed plates and the plates are rapidly drawn apart according to the procedure described in the Haake CaBER 1 Instruction Manual available from Thermo Haake (International) of Karlsruhe, Germany. The contents of the Haake CaBER 1 Instruction manual are herein incorporated by reference. By "mid-point" is meant the point equidistant from the plates. "CaBER" stands for "Capillary Break-up Extensional Rheometer".

[0026] The procedure as used for the purposes of this description involves placing the paint between two vertically opposed 6mm diameter plates with an initial separation of 3mm. The plates are then pulled vertically apart very rapidly over a period of 50ms to a separation of from 7 to 20mm so as to create the liquid capillary filament which bridges the two plates. As a result of surface tension and draining under gravity, the filament thins and eventually divides into two separated droplets, one attached to the top plate and the other to the bottom plate. A laser micrometer is used to make a sufficient number of sequential measurements of the mid-point diameter of the filament as it thins for the purpose of determining $\delta d/\delta t$. Measurements are preferably made at a frequency of from 1 to 30 kHz over a time period of from 0.1 to 1 sec with the precise frequency and period for a particular composition being chosen by trial and error aimed at ensuring enough measurements of the mid-point diameter, d , are made to enable a reliable graph of d against time, t , to be drawn. Diameters above 700 μ m are preferably ignored to minimise initial distortions due to gravity and at least when this is done, the graph comprises a substantially linear portion. The gradient of this portion is taken to be $\delta d/\delta t$. Care is needed to move the plates at a constant velocity during their separation and in particular there should be no cushioning due to any final deceleration.

[0027] The final distance between the plates is chosen so as to produce a capillary filament whose lifetime is long enough to permit a sufficient number of valid measurements to be made for the purposes of determining $\delta d/\delta t$. For example, a final separation of about 20mm (say 19.8mm) is preferred for compositions of high Brookfield viscosity whilst a final separation of 14 to 15mm (say 14.5mm) is preferred for intermediate Brookfield viscosities and a final separation of about 8mm (say 7.9mm) is preferred for low Brookfield viscosities.

[0028] A refinement of the procedure is preferred for determining $\delta d/\delta t$ for non-Newtonian compositions. It comprises making a determination of $\delta d/\delta t$ as described above, then returning the plates quickly back to their starting position and then repeating the determination as soon as possible after the plates have been returned to the starting position. Sufficient time (usually from 0.1 to 30 sec depending on the particular composition) must be allowed for the composition to recover enough structure to be able to form a filament again. Then enough further similar repeat determinations of $\delta d/\delta t$ are made to allow the reliable construction of a graph of $\delta d/\delta t$ versus time. The graph has been discovered to produce an asymptotic value for $\delta d/\delta t$ which is more useful in predicting the spraying characteristics of the composition.

[0029] If the apparent extensional viscosity exceeds 0.5 Pa.sec, then the architectural coating composition is at best expelled as a jet or stream of large droplets which produce an excessively thick coating which sags or runs quickly down a vertical surface and at worst (eg. if the apparent extensional viscosity exceeds about 2 Pa.sec), the composition may not be expelled at all. If the apparent extensional viscosity falls below 0.05 Pa.sec, the architectural coating composition will be expelled as a fine mist which does not coat a vertical surface efficiently and which is vulnerable to being inhaled by an unprotected (usually amateur) painter or to being blown off course in breezy outdoor conditions.

[0030] For efficient sag-free coating, it is preferred that 50% by volume of the paint sprayed should be sprayed as droplets having a diameter in the range of 150 to 300 μ m (and most preferably 180 to 250 μ m). Preferably not more than 5 to 20% (preferably 8 to 15%) by volume of the paint sprayed should be sprayed as droplets having a diameter of below 100 μ m otherwise there will be unwanted dangers of the spray being inhaled or blown by the wind. It is also preferred that not more than 5 to 20% (preferably 8 to 15%) by volume of the paint sprayed should be sprayed as droplets having a diameter of above 300 μ m.

[0031] As a preferred but not sufficient condition for achieving the appropriate apparent extensional viscosity, it is preferred that the high shear viscosity of the paint at 25°C should reduce to 0.015 to 1.0 Pa.sec (preferably 0.02 to 0.12 Pa.sec) when under high shear upstream of the orifice, where high shear means say a shear rate of 10⁴/sec. Viscosity

at such shear rates can be measured by the ICI Cone and Plate viscometer as described in ASTM Test D4827- 88.

[0032] Other factors which might affect the usefulness of the spray are of course the surface tension of the paint and its density. Both are functions of the complex formulations used to make modern paints and so it is not easy to vary either. In theory, surface tension (and hence apparent extensional viscosity) can be reduced by adding detergents to a paint, but this will increase the sensitivity of the paint to water. Hence, variation of surface tension is seldom a practical option. Most architectural paints will have a surface tension at 20°C in the range of 20 to 60 (preferably 23 to 45) N.10⁻³/m.

[0033] The density of paints is strongly influenced by their concentrations of heavy inorganic opacifiers such as rutile titanium dioxide (which also serves as a white pigment) or of coloured pigments or extenders such as calcium or magnesium carbonates or clays. Pigment and extender concentrations are carefully chosen to give colours having a precise hues, chromas or lightnesses, so varying their concentrations merely to adjust density is also seldom a practical option. In short, density cannot be significantly varied without unacceptable consequences for opacity and colour and the eye is very sensitive to variations in colour. Generally the density of an aqueous paint is from 1.1 to 1.6kg/litre for compositions having solids contents above 30wt%.

[0034] In the performance of this invention, paint is provided in a reservoir which can be pressurised by the hand compressor so as to pump paint via a hose through a nozzle to an outlet orifice formed in the nozzle from which the paint is sprayed. The circumference of orifice is preferably circular, but may be oblate. Preferably, the orifice has a longest diameter of from 0.5 to 2 (preferably 0.7 to 1.3 mm) and an axial length of preferably from 0.2 to 1 mm and most preferably 0.3 to 0.7mm.

[0035] It is also preferred to impart a transverse force to the paint as it passes through the nozzle so as to rotate the paint flow causing it to pass through the orifice with an essentially helical swirling motion which increases the shear forces on the paint which in turn is believed to assist the atomisation of the flow into a spray of appropriately sized droplets. By "transverse" is meant at an angle to the overall direction of travel of the composition from its entry into the nozzle to its exit via the orifice.

[0036] The transverse force may be imparted for example by means of a reaction from a surface inclined at an angle (preferably 25° to 65°) to the overall direction of flow of the coating composition through the nozzle, that is to say the inclined to the longitudinal axis of the nozzle. Suitable surfaces may be provided by one or more helical lands (akin to the rifling in a gun) located within an elongated portion of the nozzle which portion extends upstream. However, the preferred means for providing a suitable reaction comprises an annular ring into which have been cut a plurality (preferably 3 or 4) of essentially (ie. at least partially) tangential grooves which extend from the outer circumference of the annulus to its inner circumference. The grooves are preferably 0.5 to 1.5mm wide and the inner and outer radii of the annulus are preferably from 4 to 6mm and from 5 to 7mm respectively provided of course that the outer radius is larger than the inner. The grooved annulus is preferably made integral with the nozzle whereby the nozzle and annulus form part of the same unitary component and the unitary component does not rotate so that the transverse force comes from the surface without assistance from any fluid coupling. Preferably the grooved annulus receives paint from the pressurised reservoir via partial annular gaps formed in a disc upstream of the grooves which gaps communicate with the outer ends of the grooves.

[0037] On leaving the orifice, the spray expands to define a conical shape as it travels towards the surface to be coated so allowing the coating of a wider band. The preferred maximum diameter of the cone is from 100 to 250 mm at a distance of 100 to 150 mm from the orifice so as to minimise the risk of the cone becoming irregular leading to a less even coating of the surface.

[0038] It is also preferred to pass the flow of paint through a filter as it travels from reservoir to the nozzle in order to shear and break up any agglomerates, for example agglomerates of pigments or extenders which may be present in the paint. A preferred filter comprises a mesh having rectangular apertures whose sides are from 0.8 to 1.5mm long. Paint is preferably delivered from the reservoir to the nozzle via a tandem combination of a flexible hose and a rigid lance which incorporates a trigger mechanism for stopping and starting the delivery of the paint. The various components of the delivery means all impart some shear to the paint as it passes through them and the shear will affect the paint viscosity and so must be taken into account in the design of the total spraying apparatus.

[0039] The nozzle geometry should be selected with the delivery rate of the composition in mind. It has been found that the paints compositions are best delivered at a rate of from 0.3 to 1.3 litre/minute and preferably 0.5 to 1 litre/minute. The stability of the spray can be affected by the ambient temperature which may increase or decrease the apparent extensional viscosity of the composition. It is believed that a delivery rate of from 0.6 to 0.9 l/min is the least affected by temperature changes.

[0040] Selecting optimum nozzle dimensions is a simple matter. It is suggested that to begin, nozzle dimensions should be chosen which lie in about the middle of the preferred ranges and then the dimensions can be varied possibly with variations in the pressure from the hand-pump in order to investigate how the flow and delivery rates vary with pressure for any particular paint.

[0041] Delivery of the composition via a (preferably cylindrical) plenum upstream of and leading to the outlet orifice may be optionally employed to minimise fluctuations in pressure which may accompany the operation of the hand-pump

by an amateur who may become tired as pumping proceeds. Preferably the plenum should have a dimension transverse to the flow through the nozzle of from 0.5 to 3 (especially 1.3 to 2.7) mm and a length of 0.2 to 4 (especially 0.2 to 3) mm.

[0042] This invention also provides apparatus for the non-pneumatically assisted (eg. airless) spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and wherein the apparatus comprises

a) a pressurisable reservoir containing an architectural coating composition (eg paint) having a the solids content of the at least 30wt% (preferably 35 to 65wt% and most preferably 40 to 53wt%) based on the total weight of the composition and including from 0.08 to 0.6 (preferably 0.1 to 0.4) by weight (based on the total weight of the composition) of thickener where over 50wt% (preferably at least 60wt% and most preferably at least 80wt%) of the thickener (based on the total weight of thickener) is associative thickener and the composition has a Brookfield viscosity of at least at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec and most preferably, a Brookfield viscosity of from 1 to 12 Pa.sec and

b) a nozzle in communication with the reservoir which nozzle terminates in an oblate or circular outlet orifice,

c) a hand-operated compressor capable of pressurising the composition to from 2.5 to 5 bar and

d) a pressure release valve set to release pressure from the container when the pressure reaches a value in the range 2.5 to 5.0 bar.

[0043] This invention alternatively provides apparatus for the non-pneumatically assisted (eg. airless) spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and wherein the apparatus comprises

a) a pressurisable reservoir containing an architectural coating composition (eg paint) having a the solids content of the at least 30wt% (preferably 35 to 65wt% and most preferably 40 to 53wt%) based on the total weight of the composition and the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec and a Brookfield viscosity of at least 0.5 Pa.sec,

b) a nozzle in communication with the reservoir which nozzle terminates in an outlet orifice,

c) a hand-operated compressor capable of pressurising the composition to from 2.5 to 5 bar and

d) a pressure release valve set to release pressure from the container when the pressure reaches a value in the range 2.5 to 5.0 bar.

[0044] Although both the above apparatus are primarily intended for use with hand-pumps, either could employ pressures generated by low pressure domestic compressors if they are able to create pressures of 2.5 to 5 bar.

[0045] This invention further provides a viscous aqueous architectural coating composition which exhibits non-Newtonian flow and is suitable for spraying onto a surface at a pressure of from 2.5 to 5 bar to hide marks thereon which composition has a solids content of the at least 30wt% (preferably 35 to 65wt% and most preferably 40 to 53wt%) based on the total weight of the composition and including from 0.08 to 0.6 (preferably 0.1 to 0.4) by weight (based on the total weight of the composition) of thickener where over 50wt% (preferably at least 60wt% and most preferably at least 80wt%) of the thickener (based on the total weight of thickener) is associative thickener and the composition has a Brookfield viscosity of at least at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec and most preferably, a Brookfield viscosity of from 1 to 12 Pa.sec.

[0046] This invention alternatively provides a viscous aqueous architectural coating composition which exhibits non-Newtonian flow and is suitable for spraying onto a surface at a pressure of from 2.5 to bar to hide marks thereon which composition contains a binder polymer and other solid ingredients wherein the composition has a the solids content of the at least 30wt% (preferably 35 to 65wt% and most preferably 40 to 53wt%) based on the total weight of the composition and the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec and a Brookfield viscosity of at least 0.5 Pa.sec and preferably not exceeding 50 Pa.sec and most preferably, a Brookfield viscosity of from 1 to 12 Pa.sec.

Measurement of Brookfield Viscosity:

[0047] Brookfield viscosity was measured at 22°C using a Brookfield Viscometer, Model HA as supplied by Brookfield Engineering Laboratories Incorporated of Middleboro, Massachusetts. Essentially, a Brookfield Viscometer comprises a rotatable spindle which carries a disc which, when performing the measurement, is immersed into the coating composition about 10 mm below its surface. The composition should be provided in a cylindrical container having a diameter of at least 100 mm so as to avoid errors due to the proximity of the container walls.

[0048] To perform the measurement for the purposes of this description, a Brookfield No. 3 Spindle is chosen, immersed into the composition and then rotated at Brookfield Speed No 10 for at least three revolutions. The spindle is coupled

to a torque measuring device which is calibrated to express torque in terms of the viscosity of the composition either directly or after the operation of a multiplier specified by Brookfield.

Measurement of Surface Tension:

[0049] Surface tension was measured at 20°C using the De Nuoy method which employs a wire ring of wire diameter 0.44mm and ring diameter 13mm. To perform the method, the ring is positioned horizontally on the surface of the composition so that it is held by a meniscus. The ring is pulled vertically up from the meniscus and the minimum force needed to do this is measured using a spring torsion balance.

[0050] This invention and preferred embodiments of its apparatus will now be illustrated with reference to drawings in which:

Figure 1 is an exploded view in perspective showing components of a nozzle assembly for use in apparatus according to this invention,

Figure 2 is a plan view of the slotted disc shown in Figure 1,

Figure 3 is a plan view of the grooved ring shown in Figure 1,

Figure 4 is a diagrammatic representation of an apparatus incorporating a nozzle according to this invention,

Figure 5 is an exploded view in perspective showing components of an alternative nozzle assembly according to this invention,

Figure 6 is a perspective view of the alternative slotted disc shown in Figure 5,

Figure 7 is a section on the line A-A of the alternative slotted disc shown in Figure 5,

Figure 8 is a perspective view of the integral nozzle and grooved ring shown in Figure 5,

Figure 9 is a section on the line B-B of the integral nozzle and ring shown in Figure 5,

Figure 10 is an exploded view in perspective showing the components of Figure 5 when seen from the opposite direction and

Figure 11 is a section through the components shown in Figures 5 and 10 when assembled ready for use.

[0051] Figure 1 shows an exploded view of components of a nozzle assembly for use in apparatus according to this invention. The components include

i) nozzle 5 having an outer rim 5c and containing cylindrical outlet orifice 1 having a circular circumference formed in distal end 5a of protrusion 5b from nozzle 5,

ii) grooved ring 2 having upstream face 2a in which are formed three symmetrically located essentially tangential grooves 16 also shown in broken lines in Figure 3 and inclined at 45° to the longitudinal axis of nozzle 5,

iii) slotted disc 3 having three partially circumferential slots 13 located symmetrically around disc 3 adjacent the base of circumferential flange 14 which flange 14 protrudes downstream when in use and defines space 15 and

iv) filter 4 comprising wire mesh 12 and a sealing gasket 4a. In use, these components are held together in mutual contact by co-operating coupling components of the type shown as 31 and 32 in Figure 11 so that ring 2 is held within space 15 defined by flange 14 of disc 3 and the assembled combination of disc 3 and ring 2 is held within nozzle 5 by gasket 4a of filter 4 which is urged against outer rim 5c of nozzle 5 by coupling components of the type shown as 31 and 32.

[0052] To use the apparatus, paint 6 is poured into 5 litre reservoir 7 as shown in Figure 4 and a pumping pressure of 2.5 to 5 bar is generated using hand-pump 8. A flexible hose 9 leads from reservoir 7 to a valve 10 which is openable by means of trigger 10a so that on opening valve 10, paint 6 under pressure travels via rigid lance 11 through wire mesh 12 of filter 4. Wire mesh 12 filters and shears paint 6 which then leaves filter 4, travels through cylindrical elongated portion 5d of nozzle 5, encounters the upstream face of slotted disc 3 and then flows through slots 13 into grooves 16 in grooved ring 2.

[0053] Grooves 16 extend between outer and inner circumferences 18 and 17 of ring 2. As it passes through grooves 16, paint 6 (still under pressure) exerts a turning force on ring 2 causing it to rotate. Paint 6 then enters a space between ring 2 and outlet orifice 1 which is of the type defined by inner surface 25d of protruding portion 25b as shown in Figure 9. In this space, viscous fluid coupling between paint 6 and rotating ring 2 causes ring 2 to exert a transverse force on the flow of paint 6 which together with the transverse component of the direction of flow imposed on the paint by tangential grooves 16, causes and/or augments rotation (ie swirling) of flowing paint 6.

[0054] A swirling flow of paint 6 enters outlet orifice 1 through which it travels with swirling (ie a helical) motion. It is then expelled from orifice 1 whereupon it atomises and forms cone 19 of paint 6 which can be aimed at and applied to surface 20 in a coating process.

[0055] In an alternative embodiment, slotted disc 3 and rotating ring 2 are omitted and a helical motion is imparted by

helical lands (not shown) akin to the rifling in a gun which are provided within nozzle portion 5d.

[0056] Figures 5 to 11 show a more preferred embodiment of a nozzle assembly for apparatus according to the invention. In particular, Figure 5 shows cylindrical circular orifice 21 formed in distal end 25a (see Figure 10) of frustal conical portion 25b which protrudes from nozzle 25. Nozzle 25 is integral with grooved annulus 22 containing essentially tangential grooves 26 extending between outer circumference 28 and inner circumference 27 and inclined at 45° to the longitudinal axis of nozzle 25. The cylindrical space 22a (see Figure 9) defined by inner circumference 27 communicates in register with space 25c defined by inner surface 25d of conical portion 25b.

[0057] Figure 5 also shows slotted disc 23 containing four symmetrically placed partially circumferentially extending slots 23a (best seen in Figure 6) which are located adjacent the base of circumferential flange 23b which protrudes downstream when in use. Flange 23b is dimensioned so as to make a close fit in annular recess 25e formed in nozzle 25. Finally, Figure 5 also shows a filter 24 having gaskets 24a and 24b and wire mesh 24c.

[0058] Figure 11 shows the components of Figures 5 to 10 when held in their assembled positions by co-operating screw-threaded coupling components 31 and 32. Component 32 also holds lance 11 in fluid-tight communication with filter 24. Gasket 24b holds disc 23 in place in nozzle 25 upstream of and adjacent to grooves 26 with dependent flange 23b of disc 23 in place in recess 25e.

[0059] Again to use the apparatus, paint 6 is poured into 5 litre reservoir 7 and a pumping pressure of 2.5 to 5 bar is generated using hand-pump 8. The pumping pressure serves to cause paint 6 to travel through the apparatus in the overall direction from entry into nozzle 25 to exit via orifice 21 but otherwise has no significant effect on the formation of the spray so that the process is essentially non-pneumatically assisted as would be the case with a conventional air-assisted spray.

[0060] Valve 10 is opened and paint 6 under pressure flows through flexible hose 9 and valve 10 via rigid lance 11 directly to mesh 24c of filter 24 as shown in Figure 11. Elongated nozzle portion 5d is omitted from this embodiment. Paint 6 is filtered and sheared by mesh 24c whereafter it encounters the upstream face of slotted disc 23. It then passes through partially circumferentially extending slots 23a into essentially tangential grooves 26 formed in grooved annulus 22 as a result of which a transverse reaction is exerted on the flow of paint 6 by surface 26a. The transverse reaction imparts a helical or swirling motion to the paint flow with which it travels through spaces 22a and 25c in nozzle 25. The swirling paint is then expelled from outlet orifice 21 enabling an atomised cone 19 of paint 6 to be aimed at and applied to surface 20 in a coating process.

[0061] Nozzle components may be made of metal or moulded from a thermoplastics material such as polyacetal or polypropylene.

[0062] The invention is further illustrated by the following Examples of which Examples A and B are comparative.

EXAMPLE 1

[0063] A viscous aqueous non-Newtonian paint having a solids content of 46.6 and being suitable for hiding marks on a surface was made up by mixing together the ingredients shown in Table 1. The paint contained an associative thickener and had a pH of 8 to 9. Its Brookfield viscosity, its surface tension, its apparent extensional viscosity and its density all at 22°C are also shown in Table 1. The paint also had an ICI Cone and Plate viscosity at 25° C of 0.06 Pa.sec.

[0064] The paint was filled into the 5 litre reservoir of the apparatus described with reference to Figures 5 to 11. Using the hand-pump, the paint was pressurised to 4 bar and then the valve was opened allowing the paint to be propelled from the reservoir and delivered through the flexible hose of 10 mm diameter via a valve and lance through the filter into the nozzle. A helically rotating flow of paint was expelled through the nozzle outlet orifice. The paint atomised well to give a conical spray about 200mm in diameter at a point 150mm from the orifice. The paint was sprayed onto a surface and produced an even coating capable of hiding the usual type of marks found on the external walls of domestic buildings. More efficient results were achieved if the spraying was done with an action in which the lance was moved along a looping path made up of a circular revolution combined with a lateral displacement needed to cause it to traverse the surface in a linear direction.

COMPARATIVE EXAMPLES A and B

[0065] A conventional viscous aqueous non-Newtonian paint suitable for hiding marks on a surface when applied by brush was made up by mixing together the ingredients shown under Example A in Table 1. Also, a fence paint of the type promoted by the brochure mentioned earlier was made up by mixing together the ingredients shown in Table 2. The surface tensions, apparent extensional viscosities, Brookfield viscosities and densities of the paints are shown in Table 1.

[0066] Both paints were sprayed in turn onto a surface as was done for Example 1.. The conventional mark-hiding paint (Example A) failed to spray whereas the fence paint atomised excessively to give a wide conical mist which was easily blown off course.

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TABLE 1

Ingredients	Example 1 Parts by Weight	Example A Parts by Weight	Example B See Table 2
Water	32.63	25.43	
Mineral Oil Antifoam Agent	0.31	0.45	
Maleic Anhydride/Olefin Copolymer Pigment Dispersant	1.08	1.00	
Biocides	0.67	0.80	
Benzyl Alcohol	0.9	1.00	
Anionic Surfactant	0.18	0.20	
Dolomite	3.9	3.00	
Calcined Clay	9.00	9.00	
China Clay	4.90	5.27	
Rutile Titanium dioxide	10.81	10.55	
Hydroxyethyl cellulose of medium chain length: Non-Associative Thickener	0	0.54	
Hydrophobically modified Hydroxyethyl cellulose of short chain length: Associative Thickener	0.18	0	
*Binder Polymer	32.42	34.20	
Ammonia	0.11	0.12	
"Ropaque" voided polymeric pigment	2.69	7.60	
**Acrysol TT615	0.20	0	
Properties			
Wt% Solids	46.56	48.65	10.1
Surface Tension 10 ⁻³ N/m	39.9	40.6	40
Brookfield viscosity Pa.sec	4.6	16	0.06
***Apparent Extensional Viscosity Pa.sec	0.3	3	0.025
Final Plate Separation mm	7.9	19.8	7.9
Density kg/l	1.24	1.27	1.03
* The binder polymer is an aqueous latex of a copolymer of 51wt% methyl methacrylate, 48wt% 2-ethyl hexylacrylate and 1wt% acrylic acid. ** Acrysol TT-615 is an alkali swellable acrylic polymer supplied as an associative thickener by the Rohm and Haas Company of Philadelphia. *** Determined by the refined method using its asymptotic value.			

TABLE 2

Ingredient	Weight %
Water	88.7
Vinyl Acetate/Vinyl "Versate" copolymer	4.4
* Acrysol TT-615 Associative Thickener	0.5
Pigments	2.9
Wax Emulsion	2.3

(continued)

Ingredient	Weight %
Biocides	0.5
Coalescing solvent, ammonia and defoamer	0.7
Total Solids Content	10.1

Claims

1. A process for the non-pneumatically assisted spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and contains a binder polymer and other solid ingredients and which process comprises expelling the composition under pressure from an orifice formed in a nozzle wherein:
 - a) the solids content of the composition is at least 30wt% of the total weight of the composition,
 - b) the composition has a Brookfield viscosity when measured at 22°C of at least 0.5 Pa.sec
 - c) the composition contains from 0.08 to 0.6 wt% based on the total weight of the composition of thickener where over 50 wt% (based on the total weight of thickener) is associative thickener,
 - d) the orifice has either an oblate or circular circumference and
 - e) the composition is subjected to a pressure of from 2.5 to 5 bar prior to expulsion from the orifice.
2. A process for the non-pneumatically assisted spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and contains a binder polymer and other solid ingredients and which process comprises expelling the composition under pressure from an orifice formed in a nozzle wherein:
 - a) the solids content of the composition is at least 30wt% based on the total weight of the composition,
 - b) the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec together with a Brookfield viscosity when measured at 22°C of at least 0.5 Pa.sec and
 - c) the composition is subjected to a pressure (conveniently generated by a hand-pump) of from 2.5 to 5 bar prior to expulsion from the orifice.
3. A process as claimed in Claim 1 wherein the coating composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec.
4. A process as claimed in Claim 2 wherein the coating composition contains from 0.08 to 0.6 wt% (based on the total weight of the composition) of thickener where at least 60 wt% of the thickener (based on the total weight of thickener) is an associative thickener and the orifice has an oblate or circular circumference
5. A process as claimed in any one of the preceding Claims wherein the coating composition has a solids content of from 40 to 53wt%.
6. A process as claimed in any one of the preceding Claims wherein the coating composition has an apparent extensional viscosity of from 0.1 to 0.4 Pa.sec.
7. A process as claimed in any one of the preceding Claims wherein the coating composition has a Brookfield viscosity when measured at 22°C of from 1 to 12 Pa.sec.
8. A process as claimed in any one of the preceding Claims wherein the coating composition has an ICI Cone & Plate viscosity when measured at 25°C of from 0.015 to 1.0 Pa.sec.
9. A process as claimed in any one of the preceding Claims wherein a transverse force is imparted to the composition as it passes through the nozzle causing it to enter the orifice with a swirling motion.
10. A process as claimed in Claim 9 wherein the transverse force is imparted by reaction from a surface inclined at an angle to the longitudinal axis of nozzle.

11. A process as claimed in Claim 10 wherein the surface is inclined at an angle of from 25° to 65° to the longitudinal axis of the nozzle.
12. A process as claimed in Claim 10 or Claim 11 wherein the surface which imparts the reaction forms part of a groove through which the coating composition passes.
13. A process as claimed in any one of Claims 10 to Claim 12 wherein the coating composition is fed to the surface which imparts the reaction via at least one partially circumferential slot upstream of and adjacent to the surface.
14. A process as claimed in any 1 of Claims 10 to Claim 11 wherein the surface which imparts the reaction is provided by at least one helical land provided in a cylindrical portion of the nozzle.
15. A process as claimed in any one of Claims 10 to 14 wherein the coating composition passes through a frustral conical space located between the surface which imparts the reaction and the orifice.
16. A process as claimed in any one of the preceding Claims wherein the 50% by volume of the paint sprayed is sprayed as droplets having a diameter in the range of 150 to 300µm.
17. A process as claimed in any one of the preceding Claims wherein the coating composition is passed through a filter.
18. A process as claimed in any one of the preceding Claims wherein the coating composition is delivered from the orifice at a rate of from 0.3 to 1.3 litre/minute.
19. Apparatus for the non-pneumatically assisted spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and wherein the apparatus comprises
 - a) a pressurisable reservoir containing an architectural coating composition having a the solids content of the at least 30wt% based on the total weight of the composition and including from 0.08 to 0.6 by weight (based on the total weight of the composition) of thickener where over 50wt% of the thickener (based on the total weight of thickener) is associative thickener and the composition has a Brookfield viscosity of at least at least 0.5 Pa.sec,
 - b) a nozzle in communication with the reservoir which nozzle terminates in an oblate or circular outlet orifice,
 - c) a hand-operated compressor capable of pressurising the composition to from 2.5 to 5 bar and
 - d) a pressure release valve set to release pressure from the container when the pressure reaches a value in the range 2.5 to 5.0 bar.
20. Apparatus for the non-pneumatically assisted (eg. airless) spray-coating of a surface with a viscous aqueous architectural coating composition suitable for hiding marks on surfaces which composition exhibits non-Newtonian flow and wherein the apparatus comprises
 - a) a pressurisable reservoir containing an architectural coating composition having a the solids content of the at least 30wt% (preferably 35 to 65wt% and most preferably 40 to 53wt%) based on the total weight of the composition and the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec and a Brookfield viscosity of at least 0.5 Pa.sec,
 - b) a nozzle in communication with the reservoir which nozzle terminates in an outlet orifice,
 - c) a hand-operated compressor capable of pressurising the composition to from 2.5 to 5 bar and
 - d) a pressure release valve set to release pressure from the container when the pressure reaches a value in the range 2.5 to 5.0 bar.
21. Apparatus as claimed in Claim 19 wherein the composition has an apparent extensional viscosity when measured at 25°C of from 0.05 to 0.5 Pa.sec.
22. Apparatus as claimed in Claim 20 wherein the orifice has an oblate or circular circumference.
23. Apparatus as claimed any one of in Claims 19, 21 or 22 wherein the circumference of the orifice has a longest diameter of from 0.5 to 2mm.
24. Apparatus as claimed in any one of Claims 19 to 23 wherein the apparatus has means for imparting a force transverse

to the longitudinal axis of the nozzle which force causes the composition to enter the orifice with a swirling motion.

25. Apparatus as claimed in Claim 24 wherein the means for imparting a transverse force to the composition comprises by a surface inclined to the longitudinal axis of the nozzle.

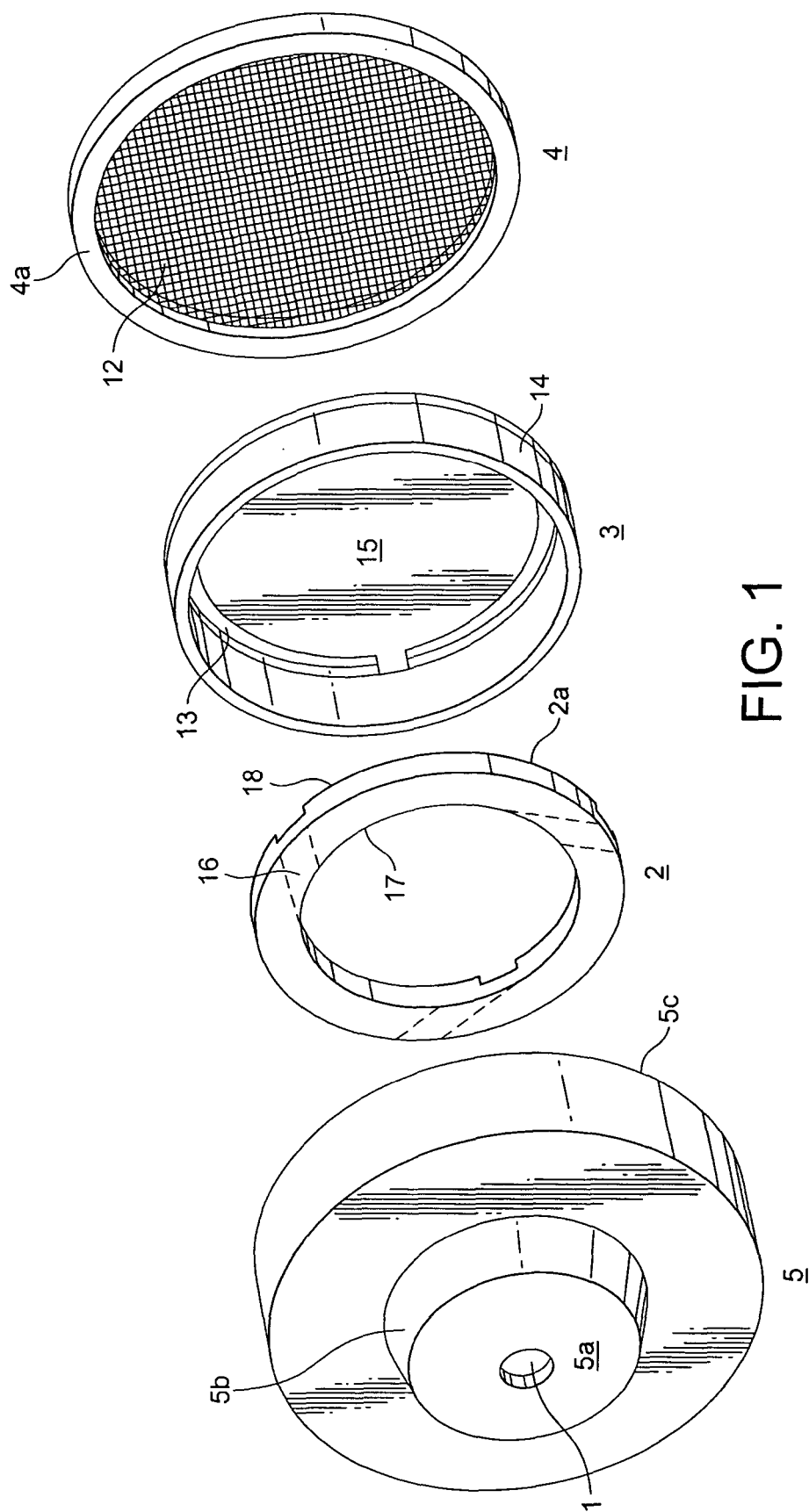
26. Apparatus as claimed in Claim 25 wherein the surface is inclined at an angle of from 25° to 65°.

27. Apparatus as claimed in any one of Claims 24 to Claim 26 wherein the apparatus comprises a component upstream of and adjacent to the surface for imparting the transverse flow which component comprises at least one partially circumferential slot through which composition can be fed to the surface.

28. Apparatus as claimed in any one of Claims 24 to 26 wherein the means for imparting a transverse force to the composition is provided by at least one helical land located in a cylindrical portion of the nozzle.

29. Apparatus as claimed in any one of Claims 19 to 28 wherein the apparatus comprises a frustral conical space located between the surface which imparts the transverse force and the orifice.

30. A viscous aqueous architectural coating composition which exhibits non-Newtonian flow and is suitable for spraying onto a surface at a pressure of from 2.5 to 5 bar to hide marks thereon which composition has a solids content of the at least 30wt% based on the total weight of the composition and including from 0.08 to 0.6 by weight (based on the total weight of the composition) of thickener where over 50wt% of the thickener (based on the total weight of thickener) is associative thickener and the composition has a Brookfield viscosity of at least 0.5 Pa.sec.



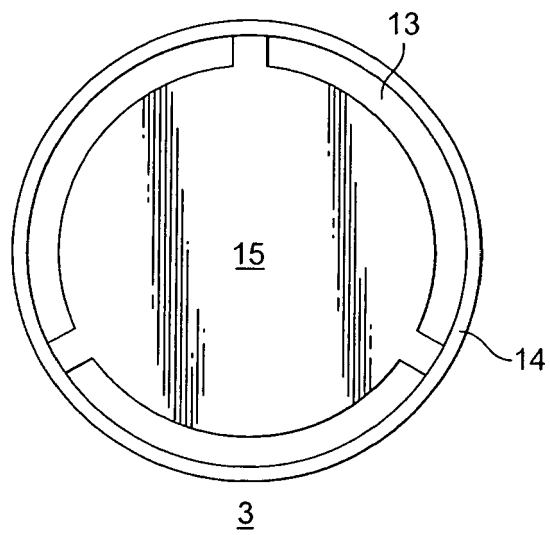


FIG. 2

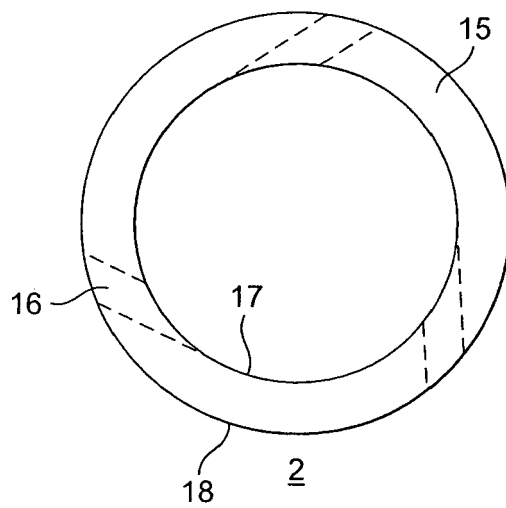


FIG. 3

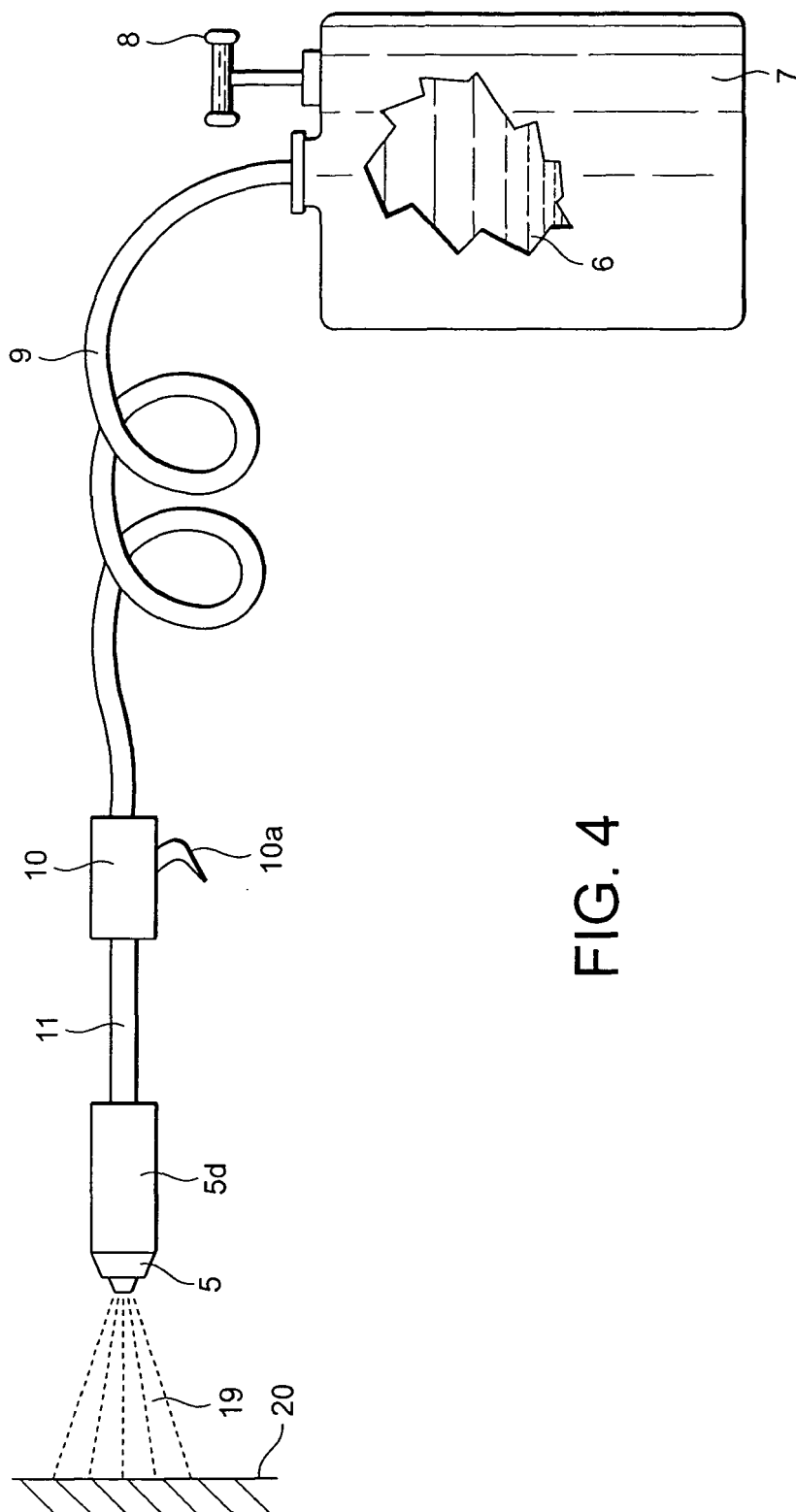


FIG. 4

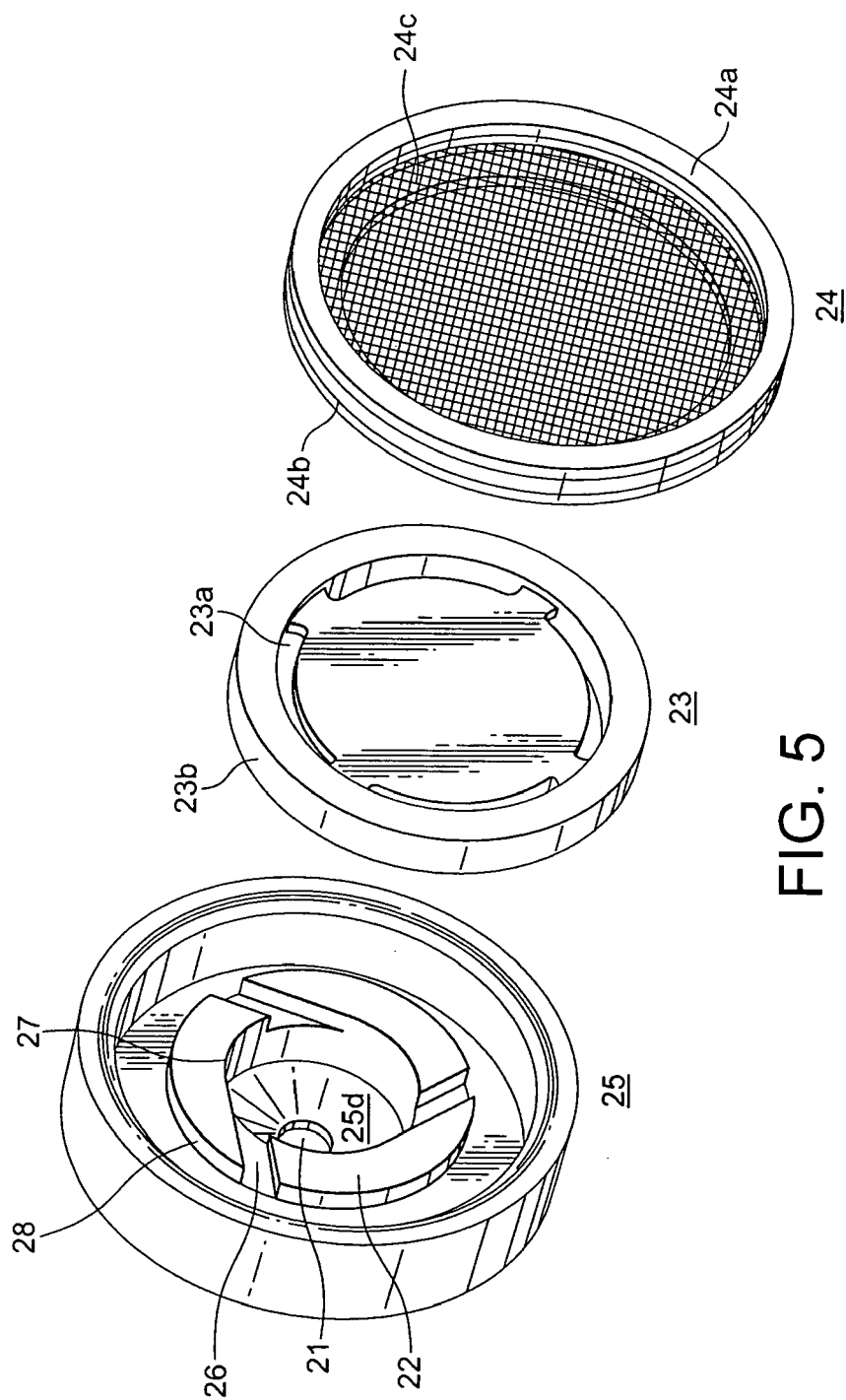


FIG. 5

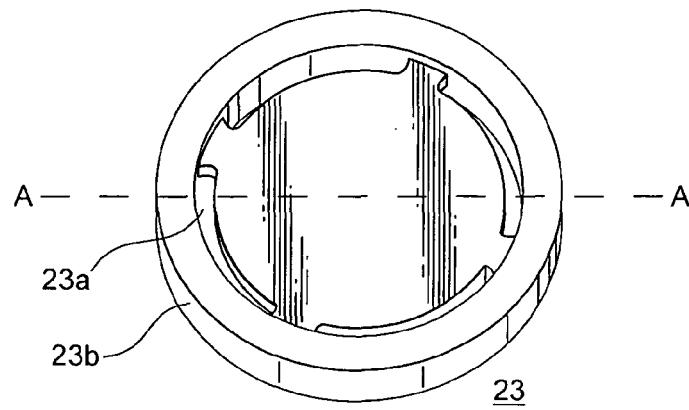


FIG. 6

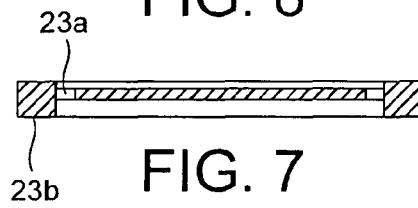


FIG. 7

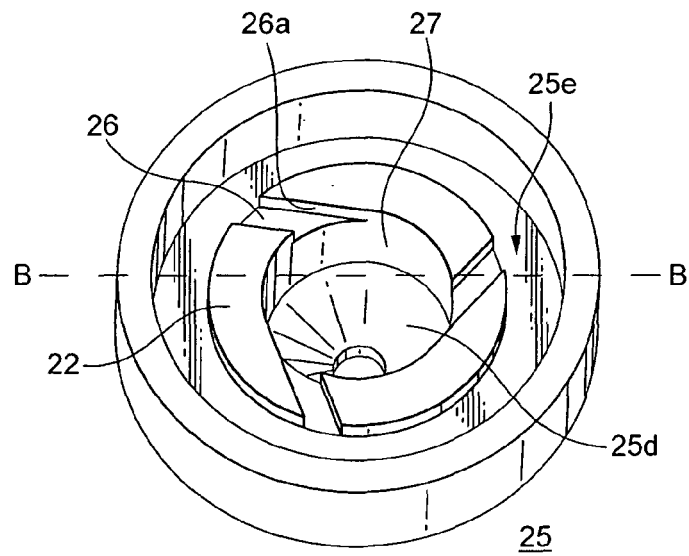


FIG. 8

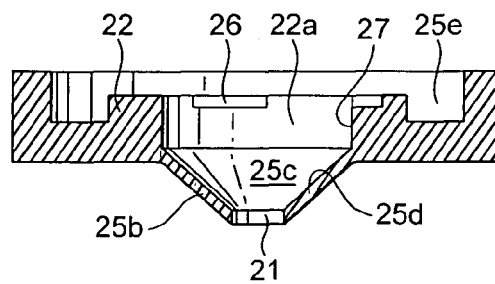
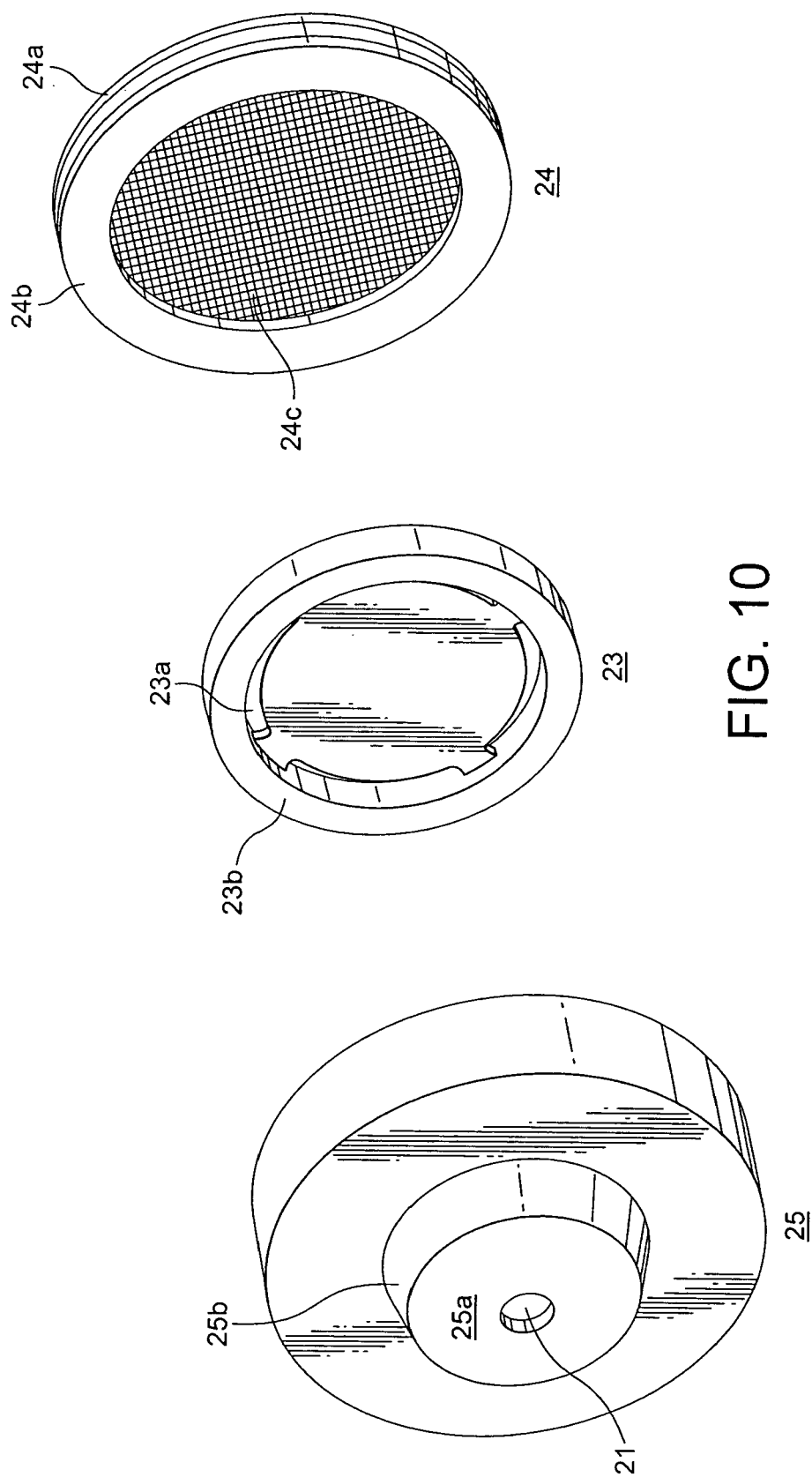


FIG. 9



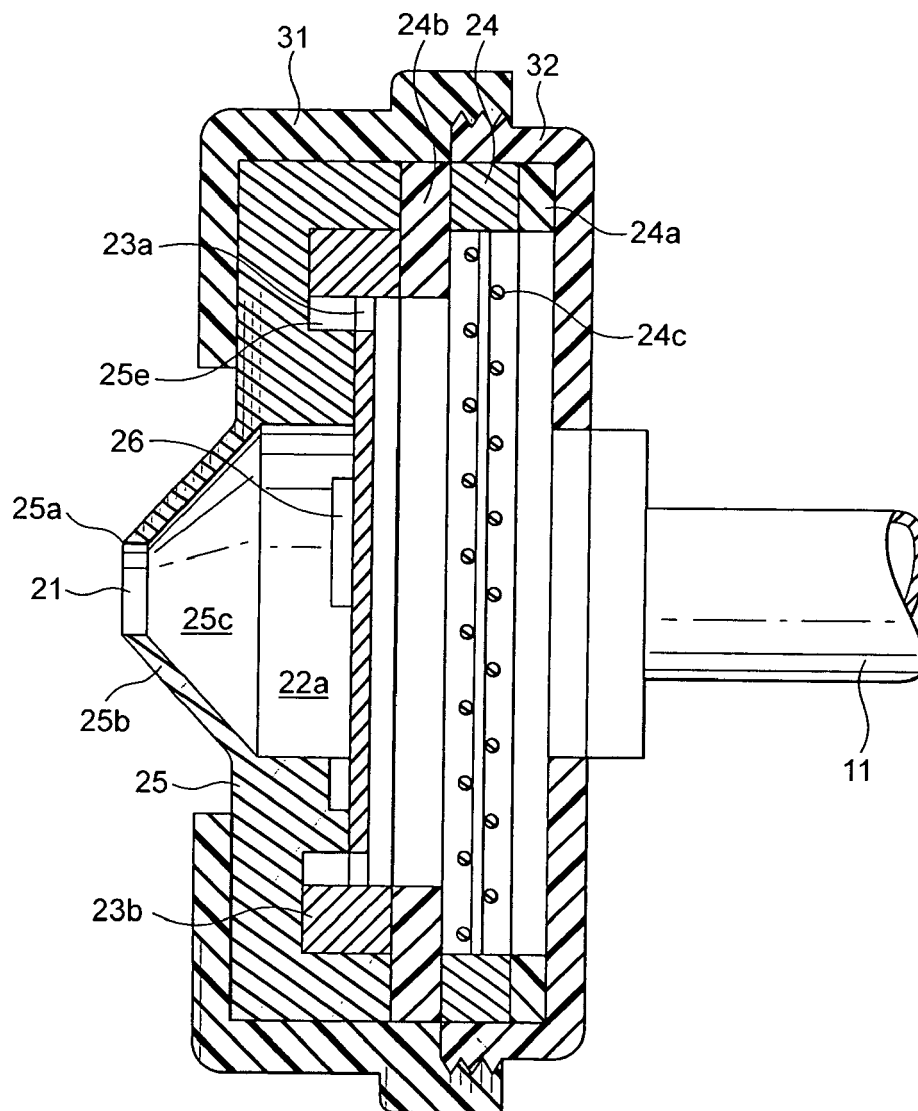


FIG. 11



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 38 0052

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Place of search The Hague		Date of completion of the search 19 September 2006	Examiner Slembrouck, Igor
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			

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