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(54) Title: COATING ON A STONE OR CERAMIC SUBSTRATE AND A COATED STONE OR CERAMIC PRODUCT

(57) Abstract: The invention relates in general level to a method for coating stone or ceramic products comprising large surface areas. The invention also relates to coated stone or ceramic products manufactured by the method. The coating is carried out by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. The invention has several both industrially and qualitatively advantageous effects such as high coating production rate, low vacuum conditions accomplishing coating of said stone or ceramic products, excellent coating properties and overall low manufacturing costs.

Coating on a stone or ceramic substrate and a coated stone or ceramic product

Field of invention

The invention relates generally to a method for coating stone or ceramic products comprising large surface areas by ultra short pulsed laser ablation. The invention also relates to products manufactured by the method. The invention has many advantageous effects such as high coating production rate, low vacuum conditions accomplishing coating of said stone or ceramic products, excellent coating properties and low manufacturing costs.

Background

Stone and ceramic products

Both exterior and interior structures of building are typically constructed from individual stone or ceramic units laid in and bound together by mortar or metal structures. The common materials of construction are brick, stone such as marble, granite, travertine, limestone, concrete block or element, glass block ant tile. Masonry is generally a high durable form of construction. However, the materials used can strongly affect the durability of the overall masonry construction. The air pollution and weather conditions in general can be harmful to certain stone and ceramic materials. For instance marble is less and less applied in construction due to its sensitivity to environmental effects. Limestone material tends instead to gather dirt, the maintenance costs in form of cleaning arising sky-high.

Above construction, stone and ceramic materials find use in for instance furniture, in chemical plants, in decorative, in machinery such as rolls on paper machine, process equipment etc.

Some of the stone qualities and especially certain colors are more desired than others. For example demand for various green stone grades is constant in Muslim societies. There is an unmet demand for example for green marble grades.

Stone products are typically large and also heavy by their nature. The adhesion of other materials is typically poor and stone material protection by for example coating is heavily limited to certain lacquers and resins. The original color and looks of the stone or similarly ceramic materials should be retained, if the color change is not specifically required.

Even though there are certain technologies emerging to deposit UV-active, self-cleaning properties owing materials such TiO_2 in nano-particle form to ceramic tiles and concrete, natural stone can not be provided with self-cleaning properties.

Laser-ablation

In the recent years, considerable development of the laser technology has provided means to produce very high-efficiency laser systems that are based on semi-conductor fibres, thus supporting advance in so called cold ablation methods.

At the priority date of the current application, solely fibrous diode-pumped semiconductor laser is competing with light-bulb pumped one, which both have the feature according to which the laser beam is lead first into a fibre, and then forwarded to the working target. These fibrous laser systems are the only ones to be applied in to the laser ablation applications in an industrial scale.

The recent fibres of the fibre lasers, as well as the consequent low radiation power seem to limit the materials to be used in the vaporization/ablation as the vaporization/ablation targets. Vaporizing/ablating aluminium can be facilitated by a small-pulsed power, whereas the more difficult substances to be vaporized/ablated as Copper, Tungsten, etc. need more pulsed power. The same applies into situation in which new compounds were in the interest to be brought up with the same conventional techniques. Examples to be mentioned are for instance manufacturing diamond directly from carbon (graphite) or alumina production straight from aluminium and oxygen via the appropriate reaction in the vapour-phase in post-laser-ablation conditions.

On one hand, one of the most significant obstacles to the forwarding progress of fibre-laser technology seems to be the fibre capabilitity of the fibre to tolerate the high power laser pulses without break-up of the fibre or without diminished quality of the laser beam.

When employing novel cold-ablation, both qualitative and production rate related problems associated with coating, thin film production as well as cutting/grooving/carving etc. has been approached by focusing on increasing laser power and reducing the spot size of the laser beam on the target. However, most of the power increase was consumed to noise. The qualitative and production rate related problems were still remaining although some laser manufacturers resolved the laser power related problem. Representative samples for both coating/thin film as well as cutting/grooving/carving etc. could be produced only with low repetition rates, narrow scanning widths and with long working time beyond industrial feasibility as such, highlighted especially for large bodies.

If the energy content of a pulse is kept constant, the power of the pulse increases in the decrease of the pulse duration, the problem with significance increases with the decreasing laser-pulse duration. The problems are significant even with the nano-second-pulse lasers, although they are not applied as such in cold ablation methods.

The pulse duration decrease further to femto or even to atto-second scale makes the problem almost irresolvable. For example, in a pico-second laser system with a pulse duration of 10-15 ps the pulse energy should be 5 μJ for a 10-30 μm spot, when the total power of the laser is 100 W and the repetition rate 20 MHz. Such a fibre to tolerate such a pulse is not available at the priority date of the current application according to the knowledge of the writer at the very date.

The production rate is directly proportional to the repetition rate or repetition frequency. On one hand the known mirror-film scanners (galvano-scanners or back and worth wobbling type of scanners), which do their duty cycle in way characterized by their back and forth movement, the stopping of the mirror at the both ends of the duty cycle is somewhat problematic as well as the accelerating and decelerating related to the turning point and the related momentary stop, which all limit the utilizability of the mirror as scanner, but especially also to the scanning width. If the production rate were tried to be scaled up, by increasing the repetition rate, the acceleration and deceleration cause either a narrow scanning range, or uneven distribution of the radiation and thus the plasma at the target when radiation hit the target via accelerating and/or decelerating mirror.

If trying to increase the coating/thin film production rate by simply increasing the pulse repetition rate, the present above mentioned known scanners direct the pulses to overlapping spot of the target area already at the low pulse repetition rates in kHz-range, in an uncontrolled way. At worst, such an approach results in release of particles from the target material, instead of plasma but at least in particle formation into plasma. Once several successive laser pulses are directed into the same location of target surface, the cumulative effect seems to erode the target material unevenly and can lead to heating of the target material, the advantages of cold ablation being thus lost.

The same problems apply to nano-second range lasers, the problem being naturally even more severe because of the long lasting pulse with high energy. Here, the target material heating occurs always, the target material temperature being elevated to approximately 5000 K. Thus, even one single nano-second range pulse erodes the target material drastically, with aforesaid problems.

In the known techniques, the target may not only wear out unevenly but may also fragment easily and degrade the plasma quality. Thus, the surface to be coated with such plasma also suffers the detrimental effects of the plasma. The surface may comprise fragments, plasma may be not evenly distributed to form such a coating etc. which are problematic in accuracy demanding application, but may be not problematic, with paint or pigment for instance, provided that the defects keep below the detection limit of the very application.

The present methods wear out the target in a single use so that same target is not available for a further use from the same surface again. The problem has been tackled by utilising only a virgin surface of the target, by moving target material and/or the beam spot accordingly.

In machining or work-related applications the left-overs or the debris comprising some fragments also can make the cut-line un even and thus inappropriate, as the case could for instance in flow-control drillings. Also the surface could be formed to have a random bumpy appearance caused by the released fragments, which may be not appropriate in certain semiconductor manufacturing, for instance.

In addition, the mirror-film scanners moving back and forth generate inertial forces that load the structure itself, but also to the bearings to which the mirror is attached and/or which cause the mirror movement. Such inertia little by little may loosen the attachment of the mirror, especially if such mirror were working nearly at the extreme range of the possible operational settings, and may lead to roaming of the settings in long time scale, which may be seen from uneven repeatability of the product quality. Because of the stoppings, as well as the direction and the related velocity changes of the movement, such a mirror-film scanner has a very limited scanning width so to be used for ablation and plasma production. The effective duty cycle is relatively short to compared the whole cycle, although the operation is anyway quite slow. In the point of view of increasing the productivity of a system utilising mirror-film scanners, the plasma production rate is in prerequisite slow, scanning width narrow, operation unstable for long time period scales, but yield also a very high probability to get involved with unwanted particle emission in to the plasma, and consequently to the products that are involved with the plasma via the machinery and/or coating.

Summary of the invention

The maintenance cost for stone and ceramic products is huge and steadily increasing and there is a great need for coating technologies for especially said products comprising large surface areas. The product lifetime should be increased and the maintenance costs should be lowered, sustainable development being a prerequisite. The coating and especially uniform coating of large stone and ceramic surfaces with one or several of the following properties: excellent optical properties, chemical and/or wear resistance, thermal resistance, coating adhesion, self-cleaning properties and possibly, even tribological properties has remained an unsolved problem.

Neither recent high-technological coating methods, nor present coating techniques related to laser ablation either in nanosecond or cold ablation range (pico-, femtosecond lasers) can provide any feasible method for industrial scale coating of stone and ceramic products comprising larger surfaces. The present CVD- and PVD-coating technologies require high-vacuum conditions making the coating process batch wise, thus non-feasible for industrial scale coating of most of the present metal products. Moreover, the distance between the stone and ceramic material to be coated and the coating material to be ablated is long, typically over 50 cm, making the coating chambers large and vacuum pumping periods time- and energy-consuming. Such high-volume vacuumed chambers are also easily contaminated with coating materials in the coating process itself, requiring continuous and time-consuming cleaning processes.

Moreover, natural stone materials don’t stand elevated and simultaneously vacuumized conditions. This is due to their chemical structure, principally all of the stone materials contain water of crystallization (water that occurs in crystals but is not covalently bonded to a host molecule or ion). Once subjected to such conditions the water evacuates and destroys the stone material structure and thus, the stone product.

While trying to increase the coating production rate in present laser-assisted coating methods in general, various defects such as pinholes, increased surface roughness, decreased or disappearing optical properties, particulates on coating surface, particulates in surface structure affecting corrosion pathways, decreased surface uniformity, decreased adhesion, unsatisfactory surface thickness and tribological properties etc. take place.

The present coating methods also drastically restrict the materials employable for coating purposes in general and thus, limit the scope of different coated stone and ceramic products available on market today.

If applicable, the target material surface is eroded in a manner that only the outmost layer of the target material can be employed for coating purposes. The rest of the material is either wasted or must be subjected to reprocessing before reuse. An aim of the current invention is to solve or at least to mitigate the problems of the known techniques.

A first object of this invention is to provide a new method how to solve a problem to coat a certain surface of a stone or ceramic product by pulsed laser deposition that so that the uniform surface area to be coated comprises at least 0.2 dm^2.

A second object of this invention is to provide stone or ceramic products being coated by pulsed laser deposition so that the coated uniform surface area comprises at least 0.2 dm^2.

A third object of this invention is to provide at least a new method and/or related means to solve a problem how to provide available such fine plasma practically from any target to be used in coating of stone or ceramic products, so that the target material do not form into the plasma any particulate fragments either at all, i.e. the plasma is pure plasma, or the fragments, if exist, are rare and at least smaller in size than the ablation depth to which the plasma is generated by ablation from said target.

A fourth object of the invention is to provide at least a new method and/or related means to solve how to coat the uniform surface area of a stone or ceramic product with the fine plasma without particulate fragments larger in size than the ablation depth to which the plasma is generated by ablation from said target, i.e. to coat substrates with pure plasma originating to practically any material.

A fifth object of this invention is to provide a good adhesion of the coating to the uniform surface area of a stone or ceramic product by said pure plasma, so that wasting the kinetic energy to particulate fragments is suppressed by limiting the existence of the particulate fragments or their size smaller than said ablation depth. Simultaneously, the particulate fragments because of their lacking existence in significant manner, they do not form cool surfaces that could influence on the homogeneity of the plasma plume via nucleation and condensation related phenomena.

A sixth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a broad scanning width simultaneously with fine plasma quality and broad coating width even for large stone or ceramic product bodies in industrial manner.

A seventh object of the invention is to provide at least a new method and/or related means to solve a problem how to provide a high repetition rate to be used to provide industrial scale applications in accordance with the objects of the invention mentioned above.

An eighth object of the invention is to provide at least a new method and/or related means to solve a problem how to provide fine plasma for coating of uniform stone or ceramic surfaces to manufacture products according to the first to seven objects, but still save target material to be used in the coating phases producing same quality coatings/thin films where needed.

A further object of the invention is to use such method and means according previous objects to solve a problem how to cold-work and/or coat surfaces for coated products. The present invention is based on the surprising discovery that stone or ceramic products comprising large surfaces can be coated with industrial production rates and excellent qualities regarding one or more of technical features such as optical transparency, chemical and/or wear resistance, scratch-free – properties, thermal resistance and/or conductivity, coating adhesion, self-cleaning properties and possibly, tribological properties, particulate-free coatings, pinhole-free coatings and electronic conductivity by employing ultra short pulsed laser deposition in a manner wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. Moreover, the present method accomplishes the economical use of target materials, because they are ablated in a manner accomplishing the reuse of already subjected material with retained high coating results. The present invention further accomplishes the coating of stone or ceramic products in low vacuum conditions with simultaneously high coating properties. Due to the problems associated with crystal water evacuation, low vacuum conditions are a prerequisite when coating natural stone or many ceramic materials. Here, the required coating chamber volumes are dramatically smaller than in competing methods. Such features decrease dramatically the overall equipment cost and increase the coating production rate. In many preferable cases, the coating equipment can be fitted into stone-cutting or ceramic tile production-line in online manner.

The coating deposition rates with 20W USPLD-apparatus are 2 mm^3/min. While increasing the laser power to 80 W, the USPLD coating deposition rate is increased to 8 mm^3/min, accordingly. According to the invention, the increase in deposition rate can now be fully employed to high quality coating production.

In this patent application the term “coating” means forming material of any thickness on a substrate. Coating can thus also mean producing thin films with thickness of e.g. < 1 µm.

Various embodiments of the inventions are combinable in suitable part.

When read and understood the invention, the skilled men in the art may know many ways to modify the shown embodiments of the invention, however, without leaving the scope of the invention, which is not limited only to the shown embodiments which are shown as examples of the embodiments of the invention.

Figures

The described and other advantages of the invention will become apparent from the following detailed description and by referring to the drawings where:

Fig 1. illustrates an exemplary galvano -scanner set-up employed in state of the art cold ablation coating/thin-film production and in machining and other work-related applications.

Fig 2. illustrates ITO-coating on polycarbonate sheet (~100 mm x 30 mm) produced by employing a prior art vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm).

Fig 3. illustrates the situation wherein prior art galvanometric scanner is employed in scanning laser beam resulting in heavy overlapping of pulses with repetition rate of 2 Mhz.

Fig 4. illustrates one embodiment of coated product according to the invention,

Fig 5. illustrates one possible turbine scanner mirror employed in method according to the invention,

Fig 6. illustrates the movement of the ablating beam achieved by each mirror in the example of Fig 5,

Fig 7. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 8. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 9. illustrates beam guidance through one possible rotating scanner to be employed according to the invention,

Fig 10a. illustrates an embodiment according to the invention, wherein target material ablated by scanning the laser beam with rotating scanner (turbine scanner).

Fig 10b. illustrates an exemplary part of target material of Figure 10a,

Fig 10c. illustrates an exemplary ablated area of target material of Figure 10b,

Fig 11a. illustrates an exemplary way according to the invention to scan and ablate target material with turbine scanner (rotating scanner),

Fig 12a. illustrates plasma-related problems of known techniques,

Fig 12b. illustrates plasma-related problems of known techniques.

Detailed Description of Embodiments of the Invention

According to the invention there is provided a method for coating a certain surface of a stone or ceramic product by laser ablation in which method the uniform surface area to be coated comprises at least 0.2 dm^2 and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

With stone or ceramic products is hereby meant but not limited to metal products such as for construction as whole, interior, exterior and decorative use, for machinery, profiles, frames, component parts, process equipment, furniture, power and energy industries, in ceramic bearings, slippery and wear-resistant tiles for wet- and icy conditions test-drive cycles, and for example ceramic tiles in space ships and laboratory use. The stone or ceramic product must not be necessarily of stone or ceramics as such. According to the invention, all the products comprising stone or ceramic surfaces regardless whether their stone or ceramic content is 100 % or 1% can be coated with now presented method. Some of the possible embodiments of the invention are illustrated in figure 4.

Ultra Short Laser Pulsed Deposition is often shortened USPLD. Said deposition is also called cold ablation, in which one of the characteristic features is that opposite for example to competing nanosecond lasers practically no heat transfer takes place from the exposed target area to the surroundings of this area, the laser pulse energies being still enough to exceed ablation threshold of target material. The pulse lengths are typically under 50 ps, such as 5 – 30 ps. i.e. ultra short, the cold ablation being reached with pico-second, femto-second and atto-second pulsed lasers. The material evaporated from the target by laser ablation is deposited onto a substrate that is held near room temperature. Still, the plasma temperature reaches 1.000.000 K on exposed target area. The plasma speed is superior, gaining even 100.000 m/s and thus, better prospective for adequate adhesion of coating/thin-film produced.

In another preferred embodiment of the invention, said uniform surface area comprises at least 0.5 dm^2. In a still preferred embodiment of the invention, said uniform surface area comprises at least 1.0 dm^2. The invention accomplishes easily also the coating of products comprising uniform coated surface areas larger than 0.5 m^2, such as 1 m^2 and over. As the process is especially beneficial for coating large surfaces with high quality plasma, it meets an underserved or especially here, unserved market of several different stone and/or ceramic products.

In industrial applications, it is important to achieve high efficiency of laser treatment. In cold ablation, the intensity of laser pulses must exceed a predetermined threshold value in order to facilitate the cold ablation phenomenon. This threshold value depends on the target material. In order to achieve high treatment efficiency and thus, industrial productivity, the repetition rate of the pulses should be high, such as 1 MHz, preferably over 2 MHz and more preferably over 5 MHz. As mentioned earlier, it is advantageous not to direct several pulses into same location of the target surface because this causes a cumulating effect in the target material, with particle deposition leading to bad quality plasma and thus, bad quality coatings and thin-films, undesirable eroding of the target material, possible target material heating etc. Therefore, to achieve a high efficiency of treatment, it is also necessary to have a high scanning speed of the laser beam. According to the invention, the velocity of the beam at the surface of the target should generally be more than 10 m/s to achieve efficient processing, and preferably more than 50 m/s and more preferably more than 100 m/s, even such speeds as 2000 m/s. However, in the optical scanners based on vibrating mirror the moment of inertia prevents achieving sufficiently high angular velocity of the mirror. The obtained laser beam at the target surface is therefore just a few m/s, figure 1 illustrating an example of such vibrating mirror, also called galvano-scanner.

As the present coating methods employing galvano-scanners can produce scanning widths at most 10 cm, preferably less, the present invention also accomplishes much more broad scanning widths such as 30 cm and even over 1 meter with simultaneously excellent coating properties and production rates.

According to one embodiment of the invention, rotating optical scanner is here meant scanners comprising at least one mirror for reflecting laser beam. Such a scanner and its applications are described in patent application FI20065867. According to another embodiment of the invention, rotating optical scanner comprises at least three mirrors for reflecting laser beam. In one embodiment of the invention, in the coating method employs a polygonal prism illustrated in figure 5. Here, a polygonal prism has faces 21, 22, 23, 24, 25, 26, 27 and 28. Arrow 20 indicates that the prism can be rotated around its axis 19, which is the symmetry axis of the prism. When the faces of the prism of the Fig. 5 are mirror faces, advantageously oblique in order to achieve scanning line, arranged such that each face in its turn will change, by means of reflection, the direction of radiation incident on the mirror surface as the prism is rotated around its axis, the prism is applicable in the method according to an embodiment of the invention, in its radiation transmission line, as part of a rotating scanner, i.e. turbine scanner. Fig. 5 shows 8 faces, but there may be considerably more faces than that, even dozens or hundreds of them. Fig. 5 also shows that the mirrors are at the same oblique angle to the axis, but especially in an embodiment including several mirrors, the said angle may vary in steps so that, by means of stepping within a certain range, a certain stepped shift on the work spot is achieved on the target, illustrated in Fig. 6, among other things. The different embodiments of invention are not to be limited into various turbine scanner mirror arrangements regarding for example the size, shape and number of laser beam reflecting mirrors.

The structure of the turbine scanner, Fig. 5, includes at least 2 mirrors, preferably more than 6 mirrors, e.g. 8 mirrors (21 to 28) positioned symmetrically around the central axis 19. As the prism 21 in the turbine scanner rotates 20 around the central axis 19, the mirrors direct the radiation, a laser beam, for instance, reflected from spot 29, accurately onto the line-shaped area, always starting from one and the same direction (Fig. 6). The mirror structure of the turbine scanner may be non-tilted (Fig. 7) or tilted at a desired angle, e.g. Figs. 8 and 9. The size and proportions of the turbine scanner can be freely chosen. In one advantageous embodiment of the coating method it has a perimeter of 30 cm, diameter of 12 cm, and a height of 5 cm.

In an embodiment of the invention it is advantageous that the mirrors 21 to 28 of the turbine scanner are preferably positioned at oblique angles to the central axis 19, because then the laser beam is easily conducted into the scanner system.

In a turbine scanner according to be employed according to an embodiment of the invention (Fig. 5) the mirrors 21 to 28 can deviate from each other in such a manner that during one round of rotational movement there are scanned as many line-shaped areas (Fig. 6) 29 as there are mirrors 21 to 28.

According to the invention, the surface to be coated can comprise whole or a part of the stone and/or ceramic product surface.

In one especially preferred embodiment of invention, stone and/or ceramic product for various uses as in construction or interior finishing, the whole sheet is coated in order to gain the preferred effect or effects of coating. One such representative product according to invention comprising a marble panel of 200 mm x 300 mm with thickness of 25 mm coated with transparent layer of Al_2O_3 is illustrated in figure 4. Here, the coated product is now resistant to weather conditions and air-pollution normally drastically decreasing the life time of uncoated marble product.
A second especially advantageous embodiment of the invention is to introduce self-cleaning, transparent TiO_2 coating to the previous embodiment of the invention.
A third especially preferred embodiment of the invention is to introduce is to introduce self-cleaning, transparent TiO_2 coating to the lime stone products employed in construction, especially in exterior use.

Marble or which ever stone material or ceramic material can according to the invention be made gas and liquid tight in several manners. In typical set-up for example for marble, the stone material is preferably preheated to approximately 200 °C, humidity and gases escaping from said stone material. This is followed by introduction of intermediate adhesive layer or direct deposition of protective layer of appropriate oxide or carbon based material. If oxide coating is preferred, such coating can according to the invention be produced by ablating oxide material, by ablating certain metal in oxygen atmosphere, or by ablating metal coating onto stone or ceramic product and oxidizing said metal coating layer in separate step by chemical means or irradiative means. Thermal oxidation can be achieved in approximately 500 °C, by RTA with lamp or by thermal oxidation in water. If conducted in this manner, the oxidation step includes the expansion of the coating, leading to transparency and tight structure.

If certain color effect is desired, such color effect can be introduced to stone or ceramic materials either before or after depositing the actual protective coating.

The coated (or uncoated) stone and ceramic product according to the invention can also be provided with a layer of polymer hybrid non-stick coating in order to enhance the cleaning properties. Additionally, it is possible to introduce self-cleaning surfaces such as UV-active TiO_2-coatings as the outer layer of the stone or ceramic product. In one preferred embodiment of the invention laser ablation is carried out under vacuum of 10^{-1} to 10^{-12} atmospheres. High vacuum conditions require quite long pumping times, and thus prolonged production times of coatings. With certain products this is not so big problem, but with for example commodity products especially comprising larger surfaces this definitely is. And with stone and ceramic materials high vacuum conditions combined with elevated temperatures are devastating.

If taking into account to for example novel wear- and scratch-free coatings, chemically inert coatings, tribological coatings, thermally resistant and/or thermally conductive coatings, electrically conductive coatings and possibly simultaneously excellent transparencies, there simply aren't any coating methods available for said products, neither from technological point of view and/or from economical point of view.

Thus, in a specially preferred embodiment of invention, the laser ablation is carried out under vacuum of 10^{-1} to 10^{-4} atmospheres. According to the invention, excellent coating/thin-film properties can be achieved already in low atmospheres, leading to dramatically decreased processing times and enhanced industrial applicability.

According to the invention it is possible to conduct the coating in a manner wherein the distance between the target material and said uniform surface area to be coated is under 25 cm, preferably under 15 cm and most preferably under 10 cm. This accomplishes the development of coating chambers with drastically diminished volumes, making the overall price of coating production lines lower and decreasing further the time required for vacuum pumping.

In a preferred embodiment of the invention the ablated surface of said target material can be repeatedly ablated in order to produce defect-free coating. In case of most of the present coating technologies, the target material wears unevenly in a manner that the affected area cannot be reused for ablation and must thus be either discarded or sent for regeneration after certain use. The problem has been tackled by developing different techniques for feeding constantly new, non-ablated target surface for coating purposes by for example moving the target material in x/y-axis or by rotating a cylinder-formed target material. The present invention accomplishes simultaneously excellent coating properties and production rates as well as use of target material in a way wherein the good quality plasma retains its quality throughout the use of substantially whole piece of target material. Preferably, more than 50% of the single target material weight is consumed to production of good quality plasma according to the invention. With good quality plasma is hear meant plasma for producing defect-free coatings and thin-films, the high quality of plasma plume being maintained at high pulse frequencies and deposition rates. Some of such properties are described here below.

According to one embodiment of the invention, the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). More preferably, the average surface roughness is less than 30 nm. With average surface roughness is here meant the average deviation from the centre line average curve fitted by a proper procedure, such as those available in AFM or profilemeter. The surface roughness affects amongst the other the wear- and scratch-free properties, tribological properties as well as the transparency of coating on metal products coated according to the invention. In certain stone and ceramic products, the surface properties of the material are rough by nature, the above said technical feature being not of same importance as in for example glass, metal or plastic derived products.

In a still preferable embodiment of the invention, the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. It can even be higher than 98%. The optical transparency of a coating in stone and/or ceramic products is especially important in uses wherein the original look of stone or ceramic material is preferred in addition to other advantages gained by the coating according to invention.

In another embodiment of the invention, produced coating on said uniform surface area contains less than one pinhole per 1 mm^2, preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area. Pinhole is a hole going through or substantially through the coating. Pinholes provide a platform for erosion of the originally coated material for example by chemical or environmental factors.

Thus, in another preferred embodiment said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm. If the early stages of the coating manufacturing process produce micrometer size particles, such particles can cause open corrosion pathways in the next layers of produced coating. Moreover, due to irregular shape of particles, it is extremely difficult to seal the surface underneath such particles. Additionally, such particles increase surface roughness substantially. The present method allows even here increased lifetime and lowered maintenance cost of different stone and/or metal products.

The stone or ceramic product itself can comprise virtually whichever stone or ceramic product. According to the invention, said uniform surface area of stone or ceramic product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. Non-limiting examples of metals include aluminum, molybdenum, titan, zirconium, copper, yttrium, magnesium, zinc, chromium, silver, gold, cobalt, tin, nickel, tantalum, gallium, manganese, vanadium, platinum and virtually whichever metal.

When producing coatings according to invention which comprise both excellent optical, wear, and scratch-free properties, especially advantageous metal oxides are for example aluminum oxide and its different composites such as aluminumtitanoxide (ATO), indiumtinoxide (ITO), yttrium stabilized zirconiumoxide.

If certain metal oxides such as titan oxide and zinc oxide are applied on surface thicknesses providing UV-activity of produced coating, the coating can possess self-cleaning properties. Such properties are highly desired in order to accomplish the use and decrease the maintenance cost of several stone and ceramic products in both interior and exterior use.

The metal oxide coatings can be produced by either ablating metal or metals in active oxygen atmosphere or by ablating oxide-materials. Even in latter possibility, it is possible to enhance the coating quality and/or production rate by conducting the ablation in oxygen atmosphere. The nitrides can be prepared in same manner in nitrogen atmosphere.

According another embodiment of the invention, said uniform surface area of stone or ceramic product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3-bonding. Such materials include for example amorphous diamond, nano-crystalline diamond or even pseudo-monocrystalline diamond. Various diamond coatings can said stone or ceramic products excellent tribological, wear- and scratch-free properties but increase also the heat-conductivity and –resistance.

In a still another embodiment of the invention, said uniform surface area of stone or ceramic product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials include boron carbon nitride, carbon nitride (both C_2N_2 and C_3N_4), boron nitride, boron carbide or phases of different hybridizations of B-N, B-C and C-N phases. Said materials are diamond-like materials having low densities, are extremely wear-resistant, and are generally chemically inert. For example carbon nitrides can be employed to protect stone or ceramic products against corrosive conditions, as coatings for medical devices and implants, battery electrodes, humidity and gas sensors, in semiconductor applications, in protecting computer hard disks, in solar cells, tools, etc.

According to one embodiment of the invention certain uniform surface area of stone or ceramic product is coated with organic polymer material. Such materials include but are not limited to chitosan and its derivatives, polysiloxanes, and different organic polymers.

By coating stone or ceramic product with chitosan there are promising perspectives to produce a new class of stone or ceramic products for both interior and exterior use. Here, polysiloxanes are especially advantageous for manufacturing products with relatively high wear-resistance and scratch-free properties with simultaneously excellent optical transparencies.

According to still another embodiment of invention said uniform surface area is coated with inorganic material. Such materials include but are not limited to for instance stone and ceramic derived materials.

In an especially preferred embodiment of the invention, different stone panels and ceramic tiles were coated by ablating a target material comprising pink agate resulting in colored but opaque coating result.

According to one embodiment of invention, said uniform surface of the stone or ceramic product is coated with only one single coating. According to another embodiment of the invention, said uniform surface of the stone or ceramic product is coated with multilayered coating. Several coatings can be produced in for different reasons. One reason might be to enhance the adhesion of certain coatings to stone or ceramic product surfaces by manufacturing a first set of coating having better adhesion to stone or ceramic surface and possessing such properties that the following coating layer has better adhesion to said layer than to stone or ceramic surface itself. Additionally, the multilayered coating can possess several functions not achievable without said structure. The present invention accomplishes the production of several coatings in one single coating chamber or in the adjacent chambers.

The present invention further accomplishes the production of composite coatings to stone or ceramic product surface by ablating simultaneously one composite material target or two or more target materials comprising one or more substances.

According to invention the thickness of said coating on uniform surface of stone or ceramic product is between 20 nm and 20 μm, preferably between 100 nm and 5 μm. The coating thicknesses must not be limited to those, because the present invention accomplishes the preparation of molecular scale coatings on the other hand, very thick coatings such as 100 μm and over, on the other hand.

The present invention further accomplishes the preparation of 3D-structures employing the stone or ceramic component as a scaffold for growing said 3D-structure.

According to the invention there is also provided a stone or ceramic product comprising a certain surface being coated by laser ablation wherein the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam. The benefits received with these products are described in more detail in the previous description of the method.

In one embodiment of the invention said uniform surface area comprises at least 0.5 dm^2. In a more preferable embodiment of the invention said uniform surface area comprises at least 1.0 dm^2. The invention accomplishes easily also the products comprising uniform coated surface areas larger than 0.5 m^2, such as 1 m^2 and over.

According to one embodiment of the invention the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm2 with Atomic Force Microscope (AFM). More preferably, the average surface roughness is less than 30 nm. With average surface roughness is here meant the average deviation from the centre line average curve fitted by a proper procedure, such as those available in AFM or profilemeter. The surface roughness affects amongst the other the wear- and scratch-free properties, tribological properties as well as the transparency of coating on stone or metal products coated according to the invention.

According to another embodiment of the invention the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%. In some cases the optical transmission can exceed 98%. The optical transparency of a coating in stone or ceramic products is especially important in uses wherein the original stone or ceramic look is preferred in addition to other gained advantages by the coating according to the invention.

According to still another embodiment of the invention said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2, preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

According to still another embodiment of the invention said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

The stone or ceramic product according to the invention can comprise virtually whichever stone or ceramic material. As mentioned earlier, the definition of stone or ceramic product in this connection must be understand in a manner, wherein the product comprises a certain stone or ceramic surface, which has been coated according to now invented method. The stone or ceramic content of the product scaffold (uncoated product) can thus vary everywhere between 0.1 to 100%.

According to one embodiment of the invention said uniform surface area of stone or ceramic product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these. The possible metals were described earlier in description of now invented coating method.

According to another embodiment of the invention said uniform surface area of stone or ceramic product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3-bonding. The possible carbon materials were described earlier in description of now invented coating method.

According to still another embodiment of the invention said uniform surface area of stone or ceramic product is coated with material comprising carbon, nitrogen and/or boron in different ratios. Such materials were described earlier in description of now invented coating method.

According to still another embodiment of the invention said uniform surface area of stone or ceramic product is coated with organic polymer material. Such materials were described earlier in more detail in description of now invented coating method.

According one embodiment of the invention said uniform surface area is coated with inorganic material. Such materials were described earlier in more detail in description of now invented coating method.

According to another preferred embodiment of the invention said uniform surface of stone or ceramic product is coated with multilayered coating. According to another preferred embodiment of the invention said uniform surface of stone or ceramic product is coated with single coating layer.

According to one preferred embodiment of the invention the thickness of said coating on uniform surface of stone or ceramic product is between 20 nm and 20 µm, preferably between 100 nm and 5 µm. The invention accomplishes also coated stone or ceramic products comprising one or several atomic layer coatings and thick coatings such as exceeding 100 µm, for example 1 mm. The present invention further accomplishes the 3D-structures prepared by employing the stone or ceramic component as a scaffold for growing said 3D-structure.

Examples

Example to demonstrate known art problems – laser technology

Figure 2 represents the ITO-coating on polycarbonate sheet (~100 mm x 30 mm) produced by employing a prior art optical scanner, namely vibrating mirror (galvo-scanner), in different ITO thin-film thicknesses (30 nm, 60 nm and 90 nm). Although the ITO-coating is not deposited on metal substrate, the picture clearly demonstrates some of the problems associated with employing vibrating mirror as an optical scanner especially in ultra short pulsed laser deposition (USPLD) but also in laser assisted coatings in general. As a vibrating mirror changes its direction of angular movement at its end positions, and due to moment inertia, the angular velocity of the mirror is not constant near to its end positions. Due to vibrating movement, the mirror continuously brakes up and stops before speeding up again, causing thus irregular treatment of the target material at the edges of the scanned area. As it can be seen from figure 2, this in turn results in low quality plasma comprising particles especially in the edges of the scanned area and finally, in low quality and seemingly uneven coating result.

The coating parameters have been selected in order to demonstrate the uneven distribution of ablated material due to the nature of employed scanner. If selecting the parameters appropriately, the film quality can be enhanced, problems becoming invisible but not excluded.

Example to demonstrate known art problems –laser technology

Conventionally galvanometric scanners are used to scan a laser beam with a typical maximum speed of about 2-3 m/s, in practice about 1 m/s. This means that even 40-60 pulses are overlapping with a repetition rate of 2 MHz (Fig. 3).

Example to demonstate known art problems – laser technology

Plasma related quality problems are demonstrated in Figure 12a and 12b, which indicate plasma generation according to known techniques. A laser pulse □ 1114 hits a target surface 1111. As the pulse is a long pulse, the depth h and the beam diameter d are of the same magnitude, as the heat of the pulse 1114 also heat the surface at the hit spot area, but also beneath the surface 1111 in deeper than the depth h. The structure experiences thermal shock and tensions are building, which while breaking, produce fragments illustrated F. As the plasma may be in the example quite poor in quality, there appears to be also molecules and clusters of them indicate by the small dots 1115, as in the relation to the reference by the numeral 1115 for the nuclei or clusters of similar structures, as formed from the gases 1116 demonstrated in the Figure 12b. The letter “o”s demonstrate particles that can form and grow from the gases and/or via agglomeration. The released fragments may also grow by condensation and/or agglomeration, which is indicated by the curved arrows from the dots to Fs and from the os to the Fs. Curved arrows indicate also phase transitions from plasma 1113 to gas 1116 and further to particles 1115 and increased particles 1117 in size. As the ablation plume in Figure 12b can comprise fragments F as well as particles built of the vapours and gases, because of the bad plasma production, the plasma is not continuous as plasma region, and thus variation of the quality may be met within a single pulse plume. Because of defects in composition and/or structure beneath the deepness h as well as the resulting variations of the deepness (Figure 12a), the target surface 1111 in Figure 12b is not any more available for a further ablations, and the target is wasted, although there were some material available.

Such problems are common with nanosecond-lasers in general, and present pico-second lasers, if they were employing the state of the art scanners.

Example of invention - 1

Figure 10a demonstrates a target material ablated with pico-second –range pulsed laser employing rotating scanner with speed accomplishing the ablation of target material with slight overlapping of adjacent pulses, avoiding the problems associated with prior art galvano-scanners. Figure 10b shows enlarged picture of one part of the ablated material, clearly demonstrating the smooth and controlled ablation of material on both x- and y-axis and thus, generation of high quality, particle-free plasma and further, high quality thin-films and coatings. Figure 10c demonstrates one example of possible x- and y-dimensions of one single ablation spot achieved by one or few pulses. Here, it can be clearly seen, that the invention accomplishes the ablation of material in a manner wherein the width of the ablated spot is always much bigger than the depth of the ablated spot area. Theoretically, the possible particles (if they would be generated) could now have a maximum size of the spot depth. The rotating scanner now accomplishes the production of good quality, particle free plasma with great production rate, with simultaneously large scanning width, especially beneficial for substrates comprising large surface areas to be coated. Furthermore, the figures 10a, 10b and 10c clearly demonstrate that opposite to present techniques, the already ablated target material area can be ablated for new generation of high class plasma – reducing thus radically the overall coating/thin-film producing cost.

Example of invention- 2

Figure 11a demonstrates an example wherein coating is carried out by employing a pico-second USPLD-laser and scanning the laser pulses with turbine scanner. Here, the scanning speed is 30 m/s, the laser spot-width being 30 µm. In this example, there is an 1/3 overlapping between the adjacent pulses.

Examples of invention – coated products

The following samples were grown on various metal substrates by employing ultra short pulsed laser deposition (USPLD) with a picosecond-range laser (X-lase, 20-80 W) at 1064 nm. Substrate temperature varied from room temperature to 250 °C and target temperature in the range of room temperature to 700 °C. Both oxide, sintered graphite, sintered graphitic $C_3N_4H_x$ (Carbodeon Ltd Oy) and various metal targets were employed. When employing oxygen atmosphere, the oxygen pressure varied n the range of 10-4 to 10-1 mbar. The employed scanner was a rotating mirror scanner accomplishing tunable velocity of the beam at the surface of the target between 1 m/s to 350 m/s. The employed repetition rates varied between 1 to 52 MHz, clearly demonstrating the importance of both the scanner and high repetition rates when producing high quality coatings in industrial manner. Deposited films were characterized by confocal microscope, FTIR and Raman spectroscopy, AFM, optical transmission measurements, ESEM and in some cases, electrical measurements (University of Kuopio, Finland; ORC, Tampere, Finland and Corelase Oy, Tampere Finland). The employed spot sizes varied between 20 to 80 μm. The wear tests were carried out by employing pin on disk-method (University of Kuopio, Finland), the tests being carried out at room temperature 22 C and 50 % (AD-coatings) or 25 % (others) relative humidity (without lubrication) with loads in the range 10-125 g using a hardened steel ball (AISI 420), 6 mm in diameter, as a pin. For AD-coatings the rotation speed was 300-600 rpm and for lenses 1 rpm. All the coatings possessed excellent wear properties as well as adhesions. Coating substrates were typically preheated to approximately 150 -250 °C in order to remove gasses and humidity from the substrate materials.

Example 1

A marble tile comprising 100 mm x 100 mm was coated by ablating sintered carbon with pulse repetition rate of 4 MHz, pulse energy 5 μJ, pulse length 20 ps and the distance between the target material and surface to be coated was 4 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform pale-brown coloured, transparent coating. The coating thickness was 500 nm and the average surface roughness was determined to be 10 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 2

A marble tile comprising 100 mm x 100 mm was coated by ablating aluminium oxide with pulse repetition rate of 4 MHz, pulse energy 4 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 3 mm. The vacuum level was 10^{-6} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was 500 nm and the average surface roughness was determined to be 5 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 3

A marble tile comprising 100 mm x 100 mm was coated by ablating aluminium oxide with pulse repetition rate of 4 MHz, pulse energy 4 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 3 mm. The coating was conducted non-vacuumized conditions. The process resulted in a uniform, transparent coating. The coating thickness was 5 µm and the average surface roughness was determined to be 105 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 4

A polished granite tile comprising 100 mm x 100 mm was coated by ablating aluminium oxide with pulse repetition rate of 4 MHz, pulse energy 4 µJ, pulse length 10 ps and the distance between the target material and surface to be coated was 9 mm. The vacuum level was 10^{-3} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was approximately 1 µm and the average surface roughness was determined to be 9 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 5

The coated granite tile of example 4 was coated with titanumdioxide by ablating titan metal in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. Pulse repetition rate was 4 MHz, pulse energy being 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 25 mm. The vacuum level was kept at 10^{-5} atmospheres before actual coating procedure. The process resulted in a uniform, transparent coating. The coating thickness was approximately 22 nm and the average surface roughness was determined to be 9 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area. The titanumdioxide coated granite tile was subjected to dirt and certain humidity. Self-cleaning properties could be detected.

Example 6

The limestone tile comprising 100 mm x 100 mm was coated with titanumdioxide by ablating titan metal in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. Pulse repetition rate was 8 MHz, pulse energy being 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 45 mm. The vacuum level was kept at 10^{-5} atmospheres before actual coating procedure. The process resulted in a uniform, transparent coating. The coating thickness was approximately 26 nm. Neither average surface roughness nor pinholes were determined. The titanumdioxide coated limestone tile was subjected to dirt and certain humidity. Self-cleaning properties could be detected.

Example 7

A marble tile comprising 100 mm x 100 mm was coated by ablating indium-tin metal target (9:1) in active oxygen atmosphere the oxygen pressure varying in the range of 10^{-4} to 10^{-1} mbar. The employed repetition rate was 4 MHz, pulse energy 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 35 mm. The vacuum level was 10^{-5} atmospheres before the reactive gas feed. The process resulted in a uniform, transparent ITO-coating. The coating thickness was 100 nm and the average surface roughness was determined to be below 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on measured area of ITO-coating. Electrical resistivity of the sample was 2.2×10^{-3} Ωcm.

Example 8

An ITO-coated marble tile of example 7 comprising 100 mm x 100 mm was coated by ablating aluminium oxide with pulse repetition rate of 4 MHz, pulse energy 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 29 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, transparent coating. The coating thickness was approximately 280 nm and the average surface roughness was determined to lower than 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 9

A polished granite tile especially to be used as slippery and wear-resistant tile for wet-and icy conditions test-drive cycles comprising 100 mm x 100 mm was coated by ablating yttrium stabilized zirconium oxide with pulse repetition rate of 8 Mhz, pulse energy 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 29 mm. The vacuum level was 10^{-5} atmospheres during the coating process. The process resulted in a uniform, opaque coating. The coating thickness was approximately 14 µm and the average surface roughness was determined to lower than 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on any measured area.

Example 10

A marble tile comprising 100 mm x 100 mm was coated by ablating yttrium aluminumoxide (YAG)-target -material. The employed repetition rate was 6 MHz, pulse energy 5 µJ, pulse length 20 ps and the distance between the target material and surface to be coated was 35 mm. The vacuum level was 10^{-5} atmospheres before the reactive gas feed. The process resulted in a uniform, transparent ITO-coating. The coating thickness was 550 nm and the average surface roughness was determined to be below 3 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM). No pinholes were found on measured area of ITO-coating.

Claims

1. A method for coating a certain surface of a stone or ceramic product by laser ablation, **characterized** in that the uniform surface area to be coated comprises at least 0.2 dm^2 and the coating is carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

2. A method according to claim 1, **characterized** in that said uniform surface area comprises at least 0.5 dm^2.

3. A method according to claim 1-2, **characterized** in that said uniform surface area comprises at least 1.0 dm^2.

4. A method according to claim 1-3, **characterized** in that the employed pulse frequency of said laser deposition is at least 1 MHz.

5. A method according to any of the preceding claims, **characterized** in that said laser ablation is carried out under vacuum of 10^{-1} to 10^{-12} atmospheres.

6. A method according to claim 5, **characterized** in that said laser ablation is carried out under vacuum on 10^{-1} to 10^{-4} atmospheres.

7. A method according to any of the preceding claims, **characterized** in that the distance between the target material and said uniform surface area to be coated is under 25 cm, preferably under 15 cm and most preferably under 10 cm.

8. A method according to any of the preceding claims, **characterized** in that the ablated surface of said target material can be repeatedly ablated in order to produce defect-free coating.

9. A method according to claim 1, **characterized** in that the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM).

10. A method according to claim 1, **characterized** in that the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%.

11. A method according to claim 1, **characterized** in that the said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2,

preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

12. A method according to claim 1, **characterized** in that said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

13. A method according to claim 1, **characterized** in that said uniform surface area of stone or ceramic product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these.

14. A method according to claim 1, **characterized** in that said uniform surface area of stone or ceramic product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3-bonding.

15. A method according to claim 1, **characterized** in that said uniform surface area of stone or ceramic product is coated with material comprising carbon, nitrogen and/or boron in different ratios.

16. A method according to claim 1, **characterized** in that said uniform surface area of stone or ceramic product is coated with organic polymer material.

17. A method according to claim 1, **characterized** in that said uniform surface area is coated with inorganic material.

18. A method according to any of the preceding claims, **characterized** in that said uniform surface of stone or ceramic product is coated with multilayered coating.

19. A method according to any of the preceding claims, **characterized** in that the thickness of said coating on uniform surface of stone or ceramic product is between 20 nm and 20 µm, preferably between 100 nm and 5 µm.

20. A stone or ceramic product comprising a certain surface being coated by laser ablation, **characterized** in that the coated uniform surface area comprises at least 0.2 dm^2 and that the coating has been carried by employing ultra short pulsed laser deposition wherein pulsed laser beam is scanned with a rotating optical scanner comprising at least one mirror for reflecting said laser beam.

21. A method according to claim 20, **characterized** in that said uniform surface area comprises at least 0.5 dm^2.

22. A method according to claim 20-21, **characterized** in that said uniform surface area comprises at least 1.0 dm^2.

23. A method according to claim 20, **characterized** in that the average surface roughness of produced coating on said uniform surface area is less than 100 nm as scanned from an area of 1 μm^2 with Atomic Force Microscope (AFM).

24. A method according to claim 20, **characterized** in that the optical transmission of produced coating on said uniform surface area is no less than 88%, preferably no less than 90% and most preferably no less than 92%.

25. A method according to claim 20, **characterized** in that the said produced coating on said uniform surface area contains less than one pinhole per 1 mm^2, preferably less than one pinhole per 1 cm^2 and most preferably no pinholes at said uniform surface area.

26. A method according to claim 20, **characterized** in that said uniform surface area is coated in a manner wherein the first 50% of said coating on said uniform surface area does not contain any particles having a diameter exceeding 1000 nm, preferably 100 nm and most preferably 30 nm.

27. A method according to claim 20, **characterized** in that said uniform surface area of stone or ceramic product is coated with metal, metal oxide, metal nitride, metal carbide or mixtures of these.

28. A method according to claim 20, **characterized** in that said uniform surface area of stone or ceramic product is coated with carbon material comprising over 90 atomic-% of carbon, with more than 70% of sp^3-bonding.

29. A method according to claim 20, **characterized** in that said uniform surface area of stone or ceramic 1 product is coated with material comprising carbon, nitrogen and/or boron in different ratios.

30. A method according to claim 20, **characterized** in that said uniform surface area of stone or ceramic product is coated with organic polymer material.

31. A method according to claim 20, **characterized** in that said uniform surface area is coated with inorganic material.

32. A method according to any of the preceding claims, **characterized** in that said uniform surface of stone or ceramic product is coated with multilayered coating.

33. A method according to any of the preceding claims, **characterized** in that the thickness of said coating on uniform surface of stone or ceramic product is between 20 nm and 20 µm, preferably between 100 nm and 5 µm.

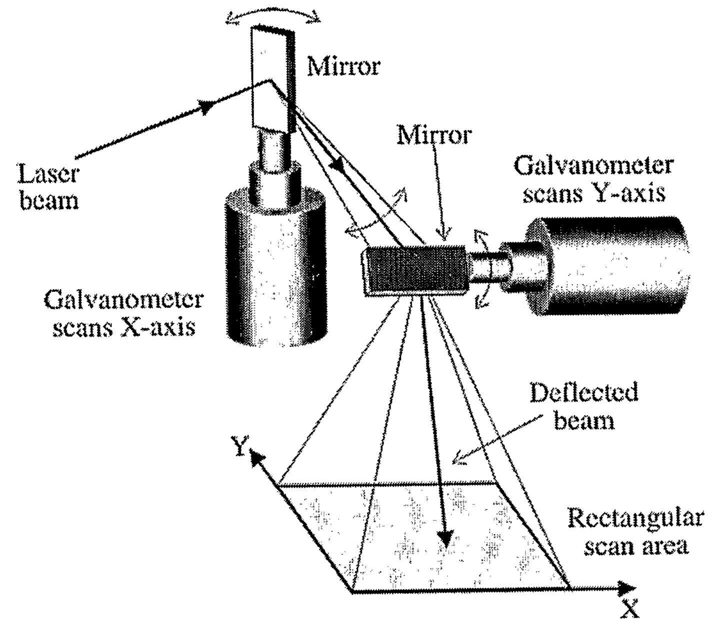


Figure 1

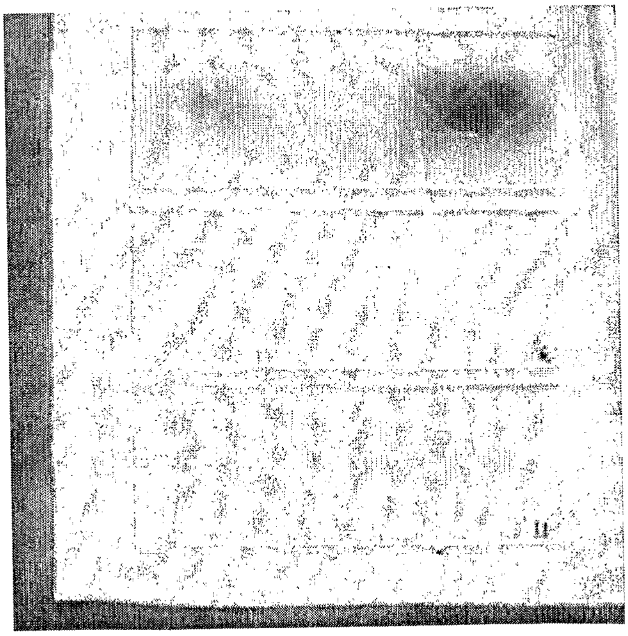


Figure 2

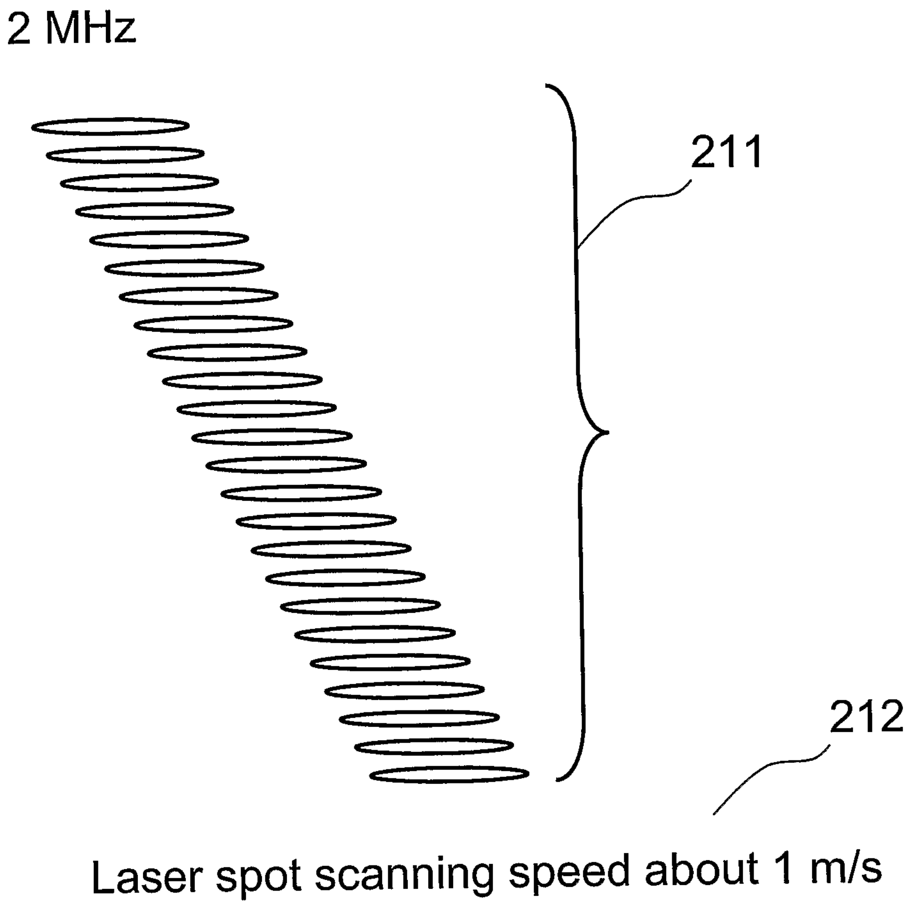


Figure 3

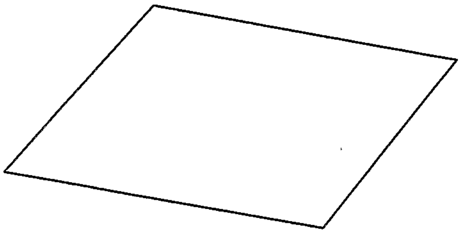


Figure 4

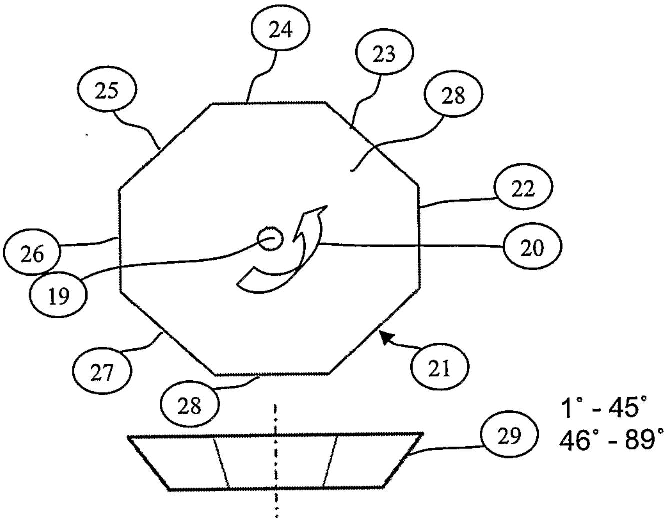
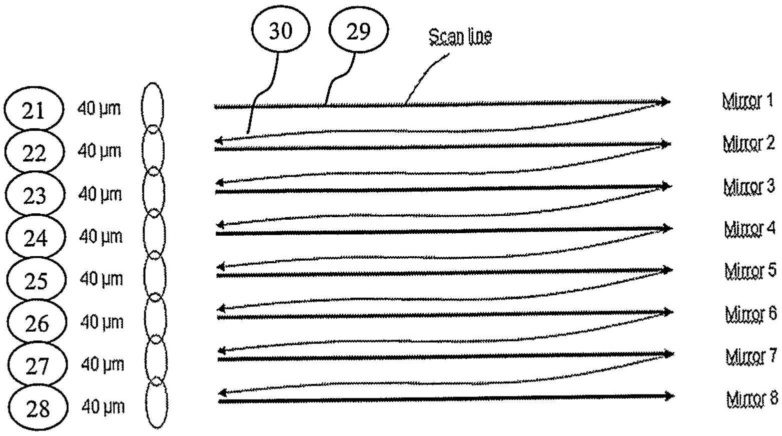


Figure 5


30
29
Scan line
21
40 µm
22
40 µm
23
40 µm
24
40 µm
25
40 µm
26
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28
40 µm
Mirror 1
Mirror 2
Mirror 3
Mirror 4
Mirror 5
Mirror 6
Mirror 7
Mirror 8

Figure 6

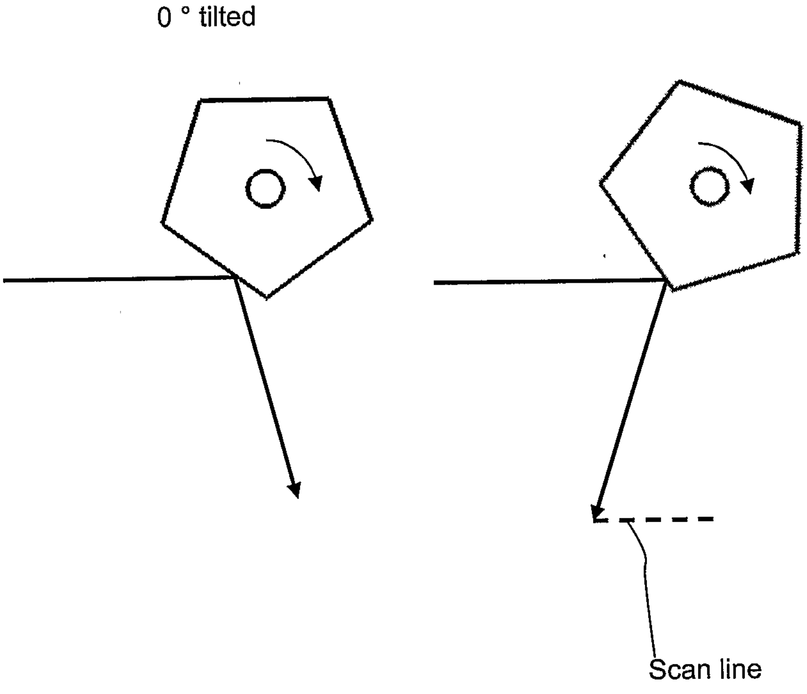

0 ° tilted
Scan line

Figure 7

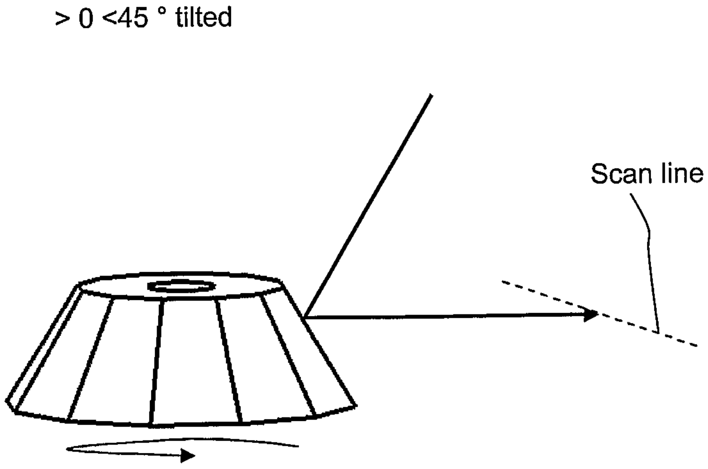


Figure 8

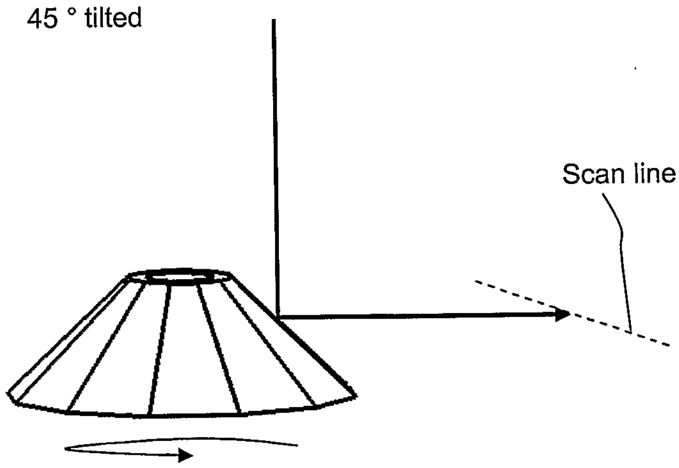


Figure 9

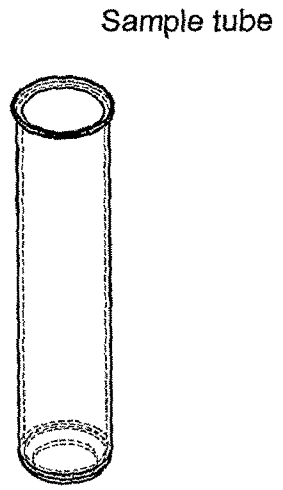
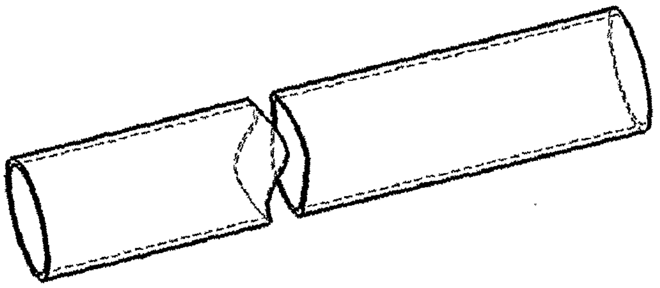


Figure 10



Plastic pipe

Figure 11

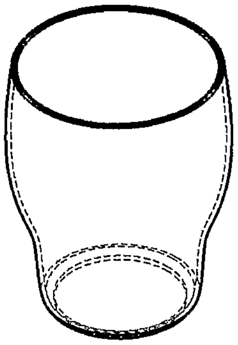


Figure 12

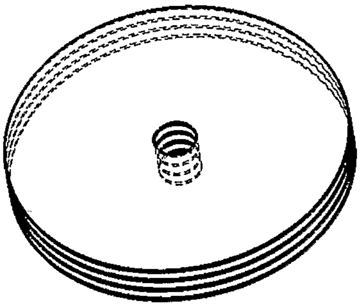


Figure 13

Plastic Mirror
surfaces

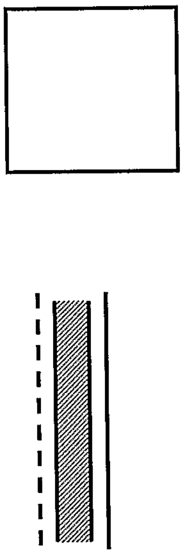


Figure 14a

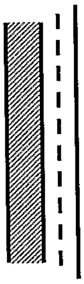


Figure 14b

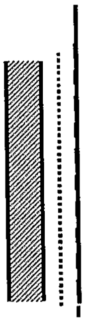


Figure 14c

Plastic shielding in airplane, train, or automobile

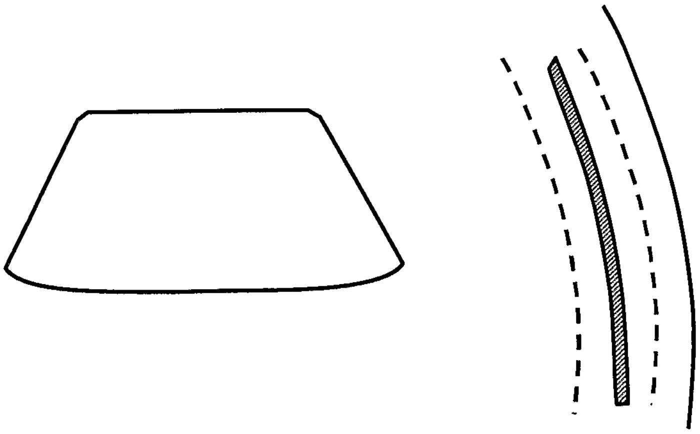


Figure 15

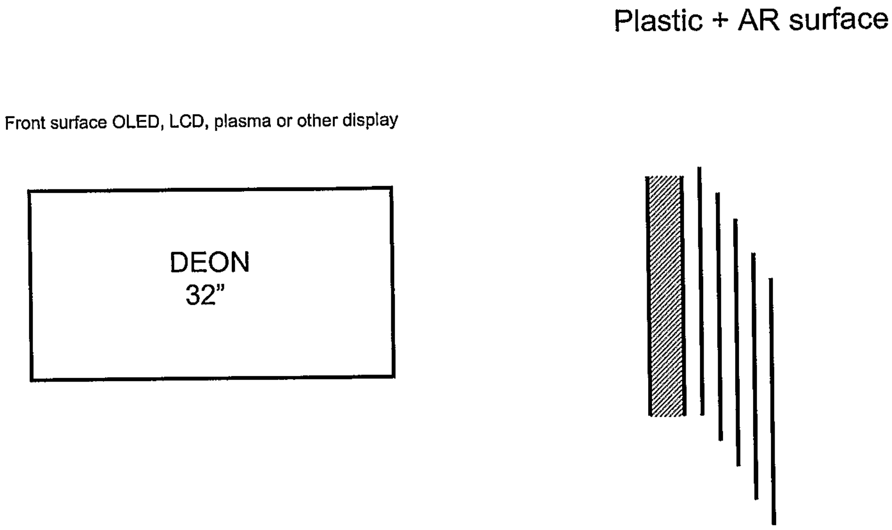


Figure 16

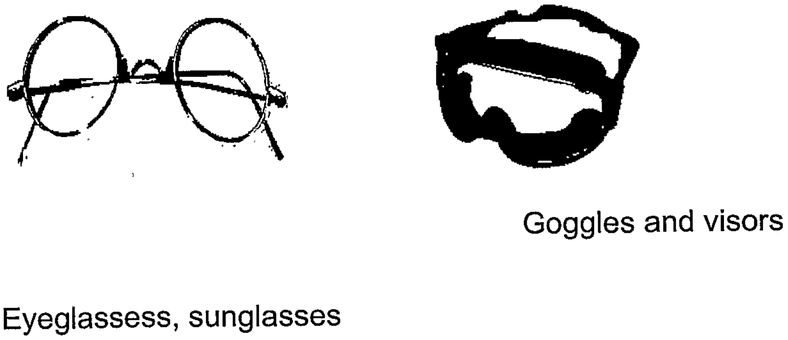


Figure 17

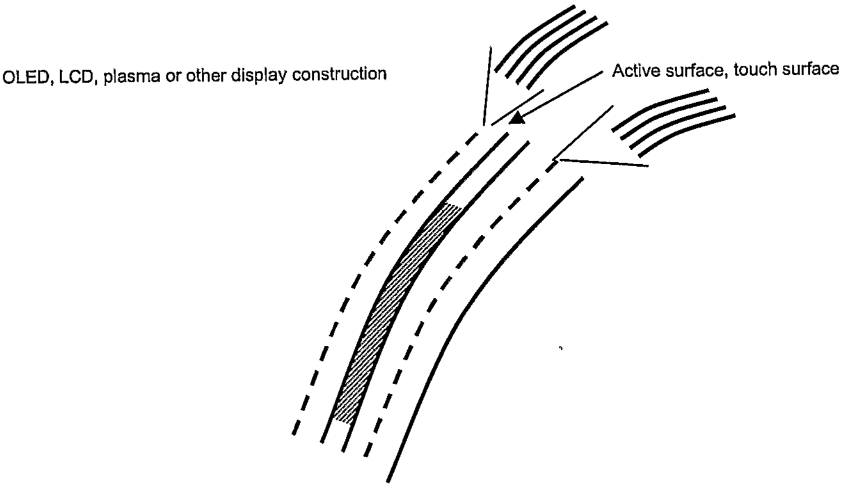


Figure 18

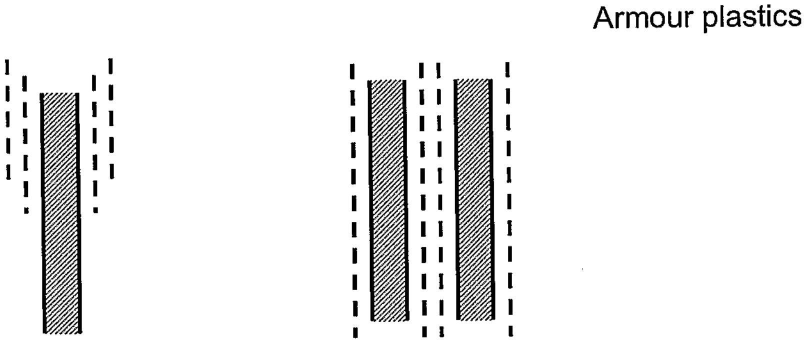


Figure 19

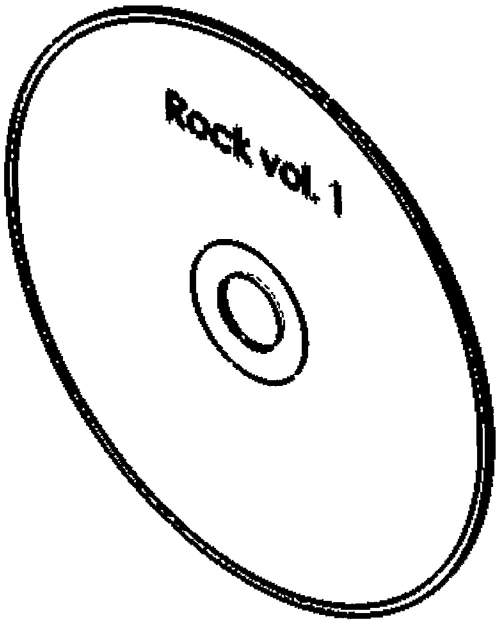


Figure 20

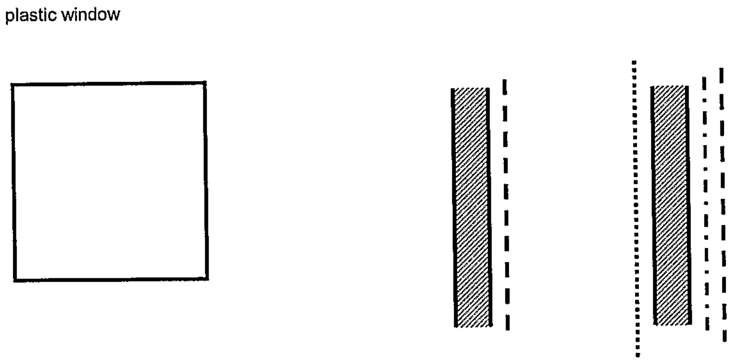


Figure 21

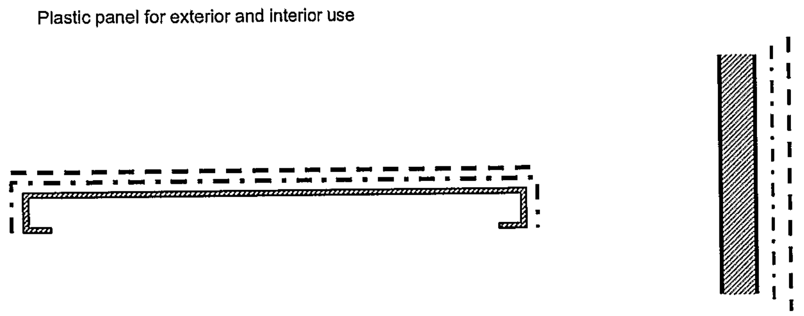


Figure 22

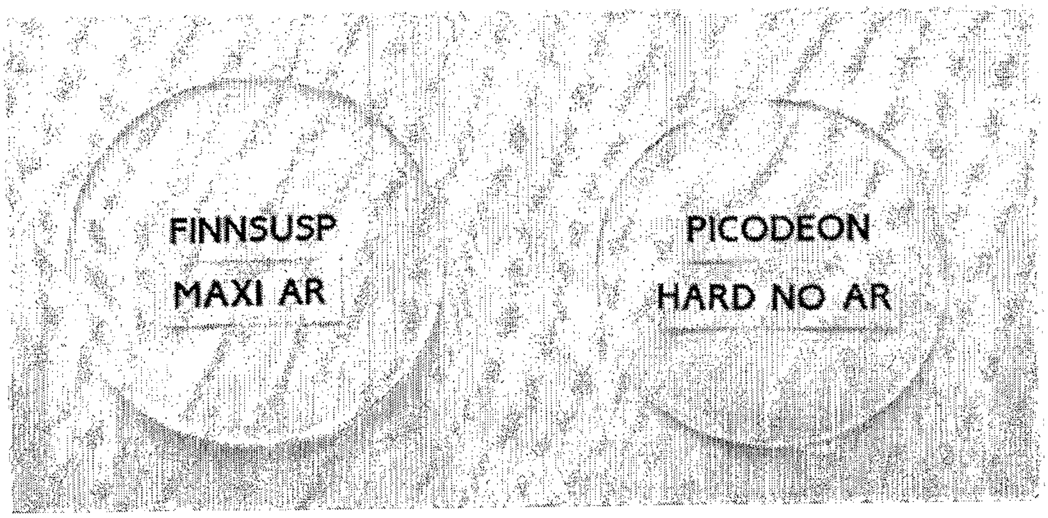


Figure 23

Figure 24

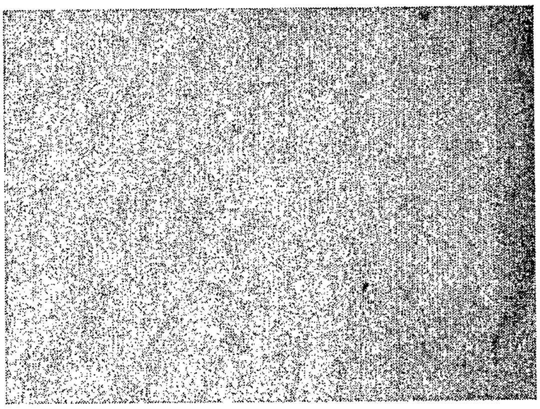


Figure 25

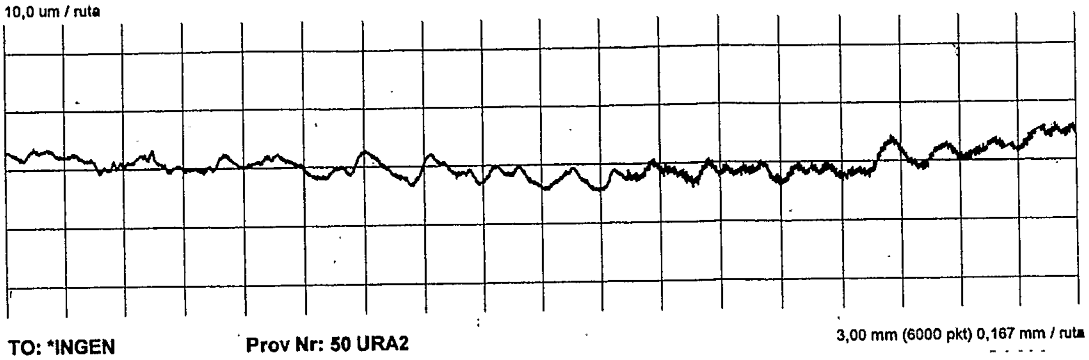


Figure 26

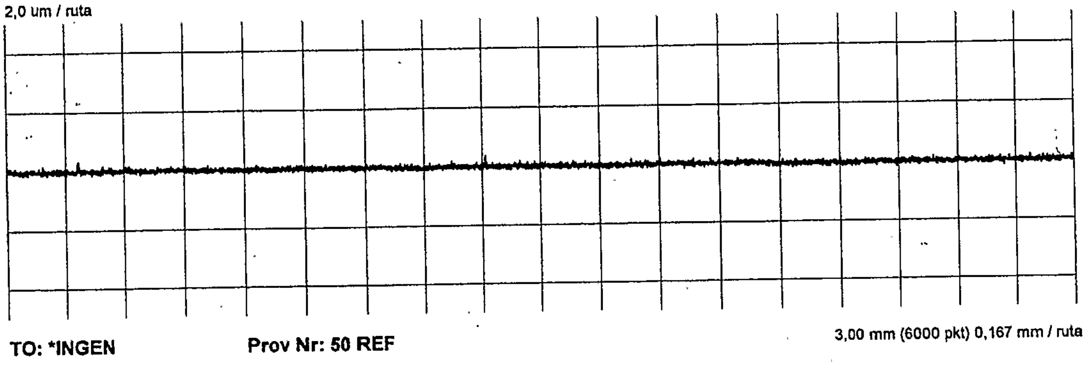


Figure 27

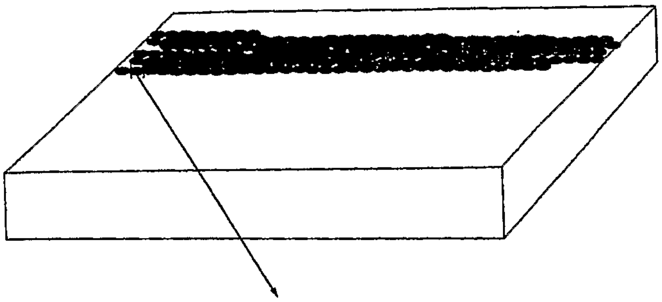


Figure 10a

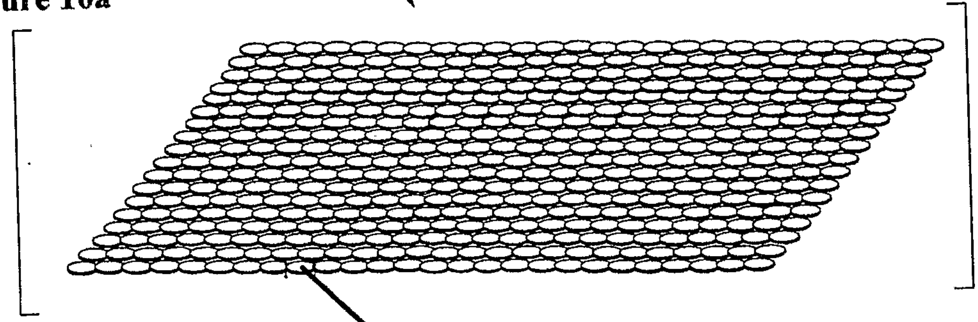


Figure 10b

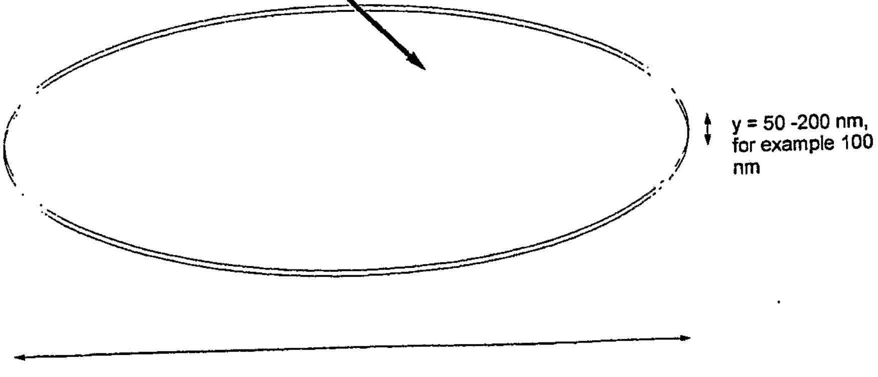


Figure 10c

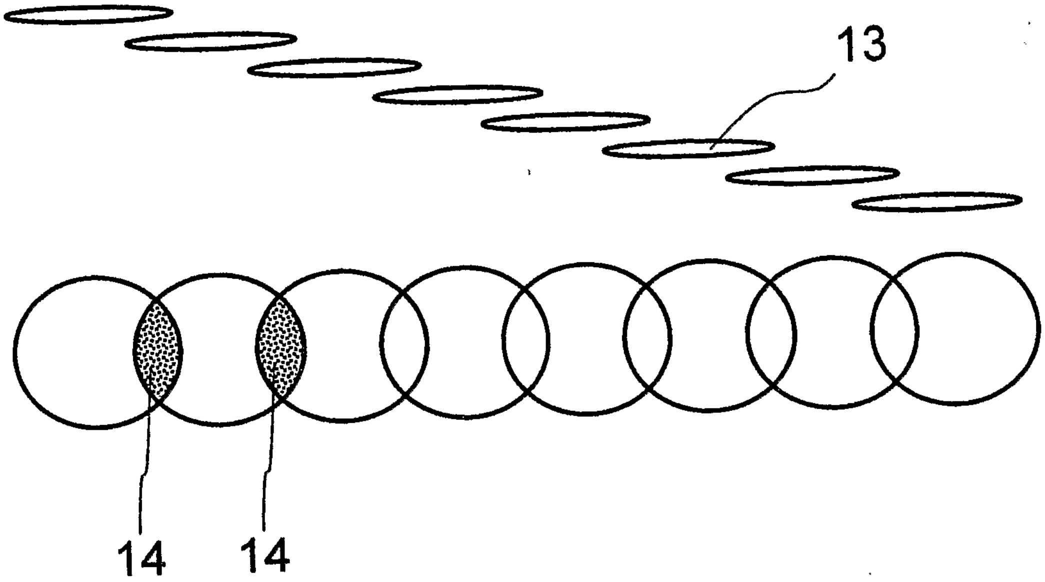


Figure 11a

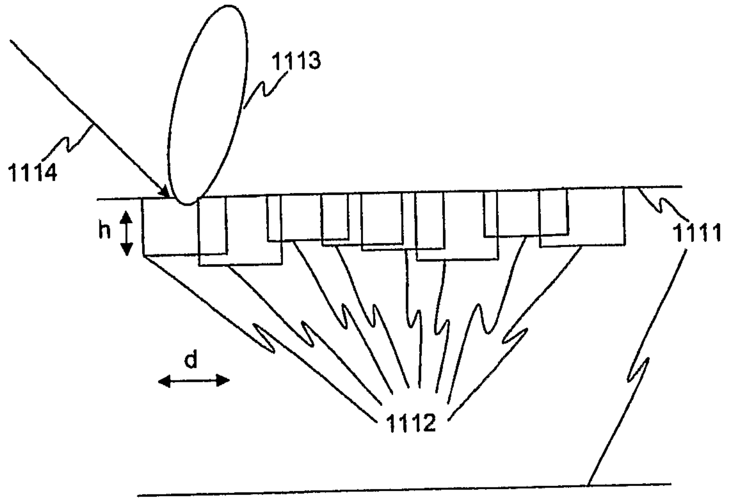


Figure 12a

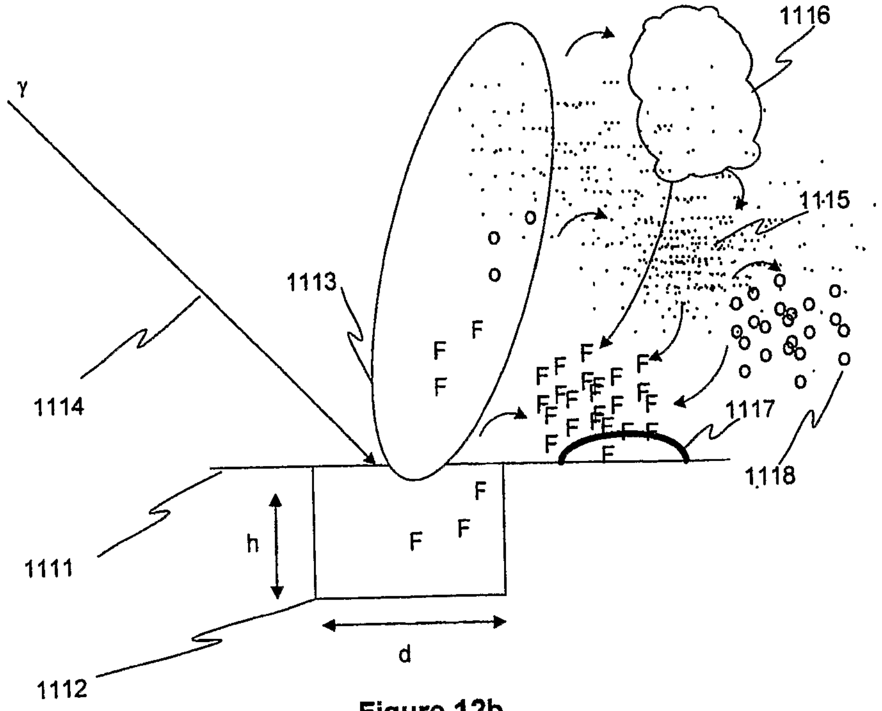


Figure 12b