(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 March 2010 (11.03.2010)

PCT

(10) International Publication Number
WO 2010/026491 A2

(51) International Patent Classification: Not classified

(21) International Application Number: PCT/IB2009/007330

(22) International Filing Date: 5 November 2009 (05.11.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
P200802558 5 September 2008 (05.09.2008) ES

(71) Applicants (*for all designated States except US*): **CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS** [ES/ES]; Serrano, 117, E-28006 Madrid (ES). **MILESMAN, S.L.** [ES/ES]; Avenida de la Libertad, 22, E-24008 Leon (ES).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **GARCIA-MORENO GONZALO, Inmaculada** [ES/ES]; Serrano, 119, E-28006 Madrid (ES). **MARTIN TORRES, Virginia** [ES/ES]; Serrano, 119, E-28006 Madrid (ES). **COSTELA GONZALES, Angel** [ES/ES]; Serrano, 119, E-28006 Madrid (ES). **GOMEZ HERNANDEZ, Clara** [ES/ES]; Serrano, 119, E-28006 Madrid (ES). **SASTRE MUNOZ, Roberto** [ES/ES]; Juan de la Cierva, 3, E-28006 Madrid (ES).

(74) Agent: **UNGRIA LÓPEZ, Javier**; Avda. Ramon y Cajal, 78, E-28043 Madrid (ES).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

— *the filing date of the international application is within two months from the date of expiration of the priority period (Rule 26bis.3)*

WO 2010/026491 A2

(54) Title: PROCEDURE TO REMOVE PIGMENTARY STAINS AND TATOOS ON THE SKIN BY A SOLID-STATE DYE LASER SYSTEM

(57) Abstract: The present invention relates to a procedure to remove pigmentary stains and tattoos on the skin, characterized in that comprises at least applying on the area to be treated a laser light emitted by a solid-state dye laser system, that tunes discrete wavelengths values comprised within the visible spectrum. Another object of the present invention is constituted by the same solid-state dye laser Irradiation system to remove pigmentary stains and tattoos on the skin according to the procedure described herein, as well as the active medium utilized in said system for generating and emitting laser light. Said active medium is characterized in that comprises at least one dye embedded in a solid matrix of at least one polymer, each dye-matrix combination emitting to a specific wavelength.

PROCEDURE TO REMOVE PIGMENTARY STAINS AND TATTOOS ON THE SKIN BY A SOLID-STATE DYE LASER SYSTEM

FIELD OF THE ART

The invention is framed in the field of Medicine, namely in the field of dermatology, and even more namely in the removal of pigmentary stains and tattoos.

STATE OF THE ART

The dye lasers are utilized nowadays in very different fields, such as industrial and medical. By way of example, in the field of Medicine this type of lasers is utilized even more profusely in different treatments and therapies, including its recent application for selective destruction of cancer cells and tissues, in the so-called Photodynamic Therapy, as well as tumor detection and diagnostic.

One of the main reasons, although among many, for which the laser utilization has reached a notable success in its medical applications, lies in the wavelength's selective effect specifically for each application. This then involves the need to ideally dispose a concrete laser for each application and treatment, which supposes a high investment in equipment, space, maintenance and personnel. Moreover, utilization of these dye lasers implies the use of a dye in liquid solution, which involves a series of drawbacks and limitations, such as:

- needing to have to employ big volumes of organic solvents, some of which are toxic, volatile and flammable;
- having to maintain a constant and regular flow of these solutions in the laser cavity;
- having to renew periodically this dye solution, when the same is degraded during its continued use, or else substitute it when it is needed to change the emission wavelength;
- tedious operations that are presented at the time of cleaning the cavity and removing said solutions, not forgetting the design and auxiliary implementation complexity to which obligates pumping said solutions in the laser cavity.

All these drawbacks suppose a series of limitations in its intensive employment, as well as its extension to other applications. So, results of great technical interest to be able to dispose dye lasers in solid state, so said drawbacks will be avoided thereby, for the advantages carrying said solid lasers over the liquid lasers, since, besides being more compact, smaller size, lighter, and therefore more manageable, allowing to work in the total absence of solutions, which is of particular importance in its clinical use, while requiring minimum maintenance, then being able to change the laser emission range in a fast and simple manner. Other additional advantages derived from the use of a solid-state laser dye, even though are not less important, are the freedom to design the laser cavity and its, in principle, low price.

On the basis of this evident interest, it has been conducted a considerable research effort, at international level, directed at both the study of photophysical and photochemical processes brought into play when the laser dyes are taken in a solid medium, as the synthesis of more efficient new dyes and laser materials and, thermal and photochemically, more stable. Although a big variety of materials has been studied such as laser dye matrixes, ranging from solidified at low temperature solutions, gelatins, molecular organic crystals, inorganic glasses ... , the polymers (organic and organic-inorganic hybrids) have presented better potential possibilities to be operable at an industrial and commercial level, as being shown by the works and results reached during the last decade (A.Costela, I.García-Moreno, R.Sastre, Materials for solid-state dye lasers, in Handbook of Advanced Electronic and Photonic Materials and Devices, Ed. Academic Press, San Diego, CA, 2001).

<u>Synthetic polymers and its utilization as an active medium is laser systems to generate laser light</u>

One of the most important sectors of application and consumption of synthetic polymers is Optics. The most common polymer applications within this field go from making conventional optical components, such as: lenses; diffraction gratings; filters; polarizers; as well as put into use in sun and corrective glasses; rigid, soft, permeable to oxygen, permanent and disposable contact lenses; even intraocular lenses that, by its biocompatibility, represent a clear example of the importance that goes beyond being a simple material, by the functions that they satisfy. Complementary examples of other developments and applications more specific are found in Optoelectronics, many of them based in non-linear optical behaviour of particular polymers. Although initially the utilization of synthetic polymers in a variety of applications in the optics field was driven, mainly, by the low cost of these materials in comparison to the traditional inorganic glasses, however, later, its utilization and consumption was extended to many other applications due to, also, a whole series of advantages over the inorganic glasses; advantages based in the intrinsic properties of these materials, as are its low weight, its easy mechanization and polishing, its greater resistance to breaking, its transformation at low temperature, etc.

However, in comparison with the conventional inorganic glasses, its main disadvantages lie, for particular applications, in its low scratching resistance and its low thermal resistance. Trying to improve these two properties of the synthetic polymers, as well as other related properties, a considerable research effort has been made directed at modifying structurally those synthetic polymers that represent a proper optical properties, mainly through: copolymerization of different monomers; by cross-linking those polymers and copolymers of proven interest for its optical properties, as well as by superficial coating and/or treatment by means of ultraviolet irradiation or electron beams. Also, new hybrid organic-inorganic polymers have been developed, following the process sol-gel, trying to bring together in the same material the properties of the organic polymers and the inorganic glasses. All of these advances and developments have allowed improving and increasing considerably the number of applications of the synthetic polymers within the field of Optics. However, specific applications impose some bigger demands even, mainly in respect to its thermal properties; properties that the polymers still are far from reaching in comparison to the ones of other conventional materials, as are, besides that of metals and ceramics, and specifically in optical applications, that of the inorganic glasses.

One characteristic of synthetic polymers, related to its thermal properties, is its insulating behavior, both thermal and electric and acoustic, characteristics which in turn are fundamental across a series of applications of these materials. This insulating characteristic is precisely that which determines the margin of use of the synthetic polymers in those optical applications in which the incident light over the same is partially absorbed, either directly, by some chromophore present in the polymer structure, or indirectly, through some additive incorporated to the same. In both cases, the absorbed energy part that is released to the environment as heat presents the inconvenience of its poor dissipation, as consequence of the insulating characteristic of those materials, which can eventually lead its thermal degradation and/or that of the incorporated additives to the same, due to the high temperatures reached locally in the zones where light incides. This inconvenience results then being a limiting factor at the moment of utilizing the synthetic polymers as solid matrixes in certain optical components, as are the optical filters, waveguides and the solid-state dye lasers, among others. In this last polymers application as generator matrix of solid-state dyes laser, where the thermal stability is a determinant factor of possible utilization of these materials at industrial and commercial scale.

One of the working directions followed to improve the photostability of these materials has consisted in developing a whole series of new polymeric matrixes, linear and cross-linked, in which by copolymerization the dye molecules were covalently introduced, in this way managing to improve the useful life of these new lasers, as well as all the above stated advantages for solid-state dye lasers (ES 9501419, 1995 and USA 6,281,315 2001).

Likewise, a systematic study has been carried out about the structural modification of dipyrromethene dye substitutes, with the objective of improving its properties and photostability. To this end, aim our efforts in establishing the effect of the substitution in the position 8 of the pyrromethene ring, introducing, both acetoxipolymethylene groups and methacryloxypolymethylene groups, that were utilized as model laser dyes and monomer laser dyes. These new dyes presented, both in liquid solution and in solid matrixes, a better laser efficiency and a more notable photostability, than the corresponding commercial laser dyes when covalently united to a polymer (ES 19990001540; A. Costela., I. García-Moreno, F. Amat-Guerri, M. Liras, R. Sastre, Appl. Phys. B, 76, 365, 2003, and M. Álvarez, F. Amat-Guerri, A. Costela, I. García-Moreno, M. Liras, R. Sastre, Appl. Phys. B, 80, 993, 2005). Next, incorporated also in said position 8 of the indaceno ring, only a acetoxi-p-phenylene polymethylene group and a methacryloxy-p-phenylene polymethylene group, of which photophysical properties and its evaluation as laser showed that, as much in liquid solution saturated to the air, as in their solid copolymers with methyl methacrylate, their laser emission efficiencies and their photostability were improved noticeably (I. García-Moreno, A. Costela, R. Sastre, F. Amat-Guerri, M. Liras, F. López-Arbeloa, J. Bañuelos, I. López-Arbeloa, J. Phys. Chem. A, 108, 3315, 2004).

- Subsequently, trying to improve the thermal properties of these polymeric matrixes, new hybrid organic-inorganic polymers were also developed, obtained by procedures of polymerization-polycondensation simultaneous synthesis, that has allowed reaching even higher photostabilities [Costela, A., García-Moreno, I., Gómez, C., García, O., Garrido, L. and Sastre, R., Highly efficient and stable doped hybrid organic-inorganic materials for solid-state dye lasers, Chem. Phys. Lett. 387: 496-501 (2004); Costela, A., García-Moreno, I., Gómez, C., García, O. and Sastre, R., Enhancement of laser properties of pyrromethene 567 dye incorporated into new organic-inorganic hybrid materials, Chem. Phys. Lett. 369: 656-661 (2003); Costela, A., García-Moreno, I., Gómez, C., García, O., and Sastre, R., Environment effects on the lasing photostability of Rhodamine 6G incorporated into organic-inorganic hybrid materials, Appl. Phys. B 78: 629-634 (2004); Costela, A., García-Moreno, I., García, O., del Agua, D. and Sastre, R., Structural influence of the inorganic network in the laser performance of dye-doped hybrid materials, Appl. Phys. B. 80: 749-755 (2005); García-Moreno, I., Costela, A., Cuesta. A., García, O., del Agua, D. and Sastre, R., Synthesis, Structure, and Physical Properties of Hybrid Nanocomposites for Solid-State Dye Lasers, J. Phys. Chem. B 109: 21618-21626 (2005)]. Likewise, trying to improve the photostability even more, at the same time as its thermo-optical and mechanical properties, other new hybrid organic-inorganic polymers were obtained coming from mesoporous silicas or aerogels, consistent in tridimensional networks of nanometric-sized open pore silica, that are inundated with the appropriate formulations of monomer-laser dyes, to subsequently be polymerized *in situ*, in a controlled manner, allowing them to obtain some more efficient materials in their laser emission and highly photostable, chiefly when the polymers obtained within the mesoporous silica matrix were of a fluorinated nature [Costela, A., García-Moreno, I., Gómez, C., García, O., Sastre, R., Roig, A., and Molins, E., Polymer-Filled Nanoporous Silica Aerogels as Hosts for Highly Stable Solid-State Dye Lasers, J. Phys. Chem B 109: 4475-4480 (2005); García, O., Sastre, R., del Agua, D., Costela, A., García-Moreno, I., and Roig, A., Efficient optical materials based on fluorinated-polymeric silica aerogels, Chem. Phys. Lett. 427: 375-378 (2006); Costela, A., García-Moreno, I., del Agua, D., García, O. and Sastre, R., Highly photostable solid-state dye lasers based on silicon-modified organic matrixes,

J. Appl. Phys. 101: 073110 (2007)]. The principal advantage that contributes the incorporation of the silica in these materials lies in substantially improving its thermal conductivity, that favors the local heat dissipation released during the dye process of excitation or pumping, thus avoiding, in great extent, the thermal dye degradation and, therefore, prolonging the service lifespan of the laser generator. So, considering the synthesis difficulties that present both polymer families, very recently set out for these applications the synthesis of new polymers in which are incorporated the silica at a molecular level [ES 200800220], which allows obtaining intrinsically more homogeneous materials than the ones obtained by other methods, improving even more its thermal conductivity and its optical properties.

All these results and developments allow obtaining some materials which are sufficiently efficient and stable as to be used at an industrial or commercial level, as active means for the emission of laser light.

At the light of the actual knowledge and developments achieved in the field of solid-state dye lasers which are described here, it is of great interest being applied the development of a new laser that is capable of being tuned to different wavelengths within the visible area of the spectrum in terms of the laser dye used, for its application in dermatological procedures, specifically, in the removal of pigmentary stains and tattoos; some of the most important applications of lasers depend, among others, though mainly, on its emission wavelength, reason for which it is of great interest and utility to develop a laser which is based on these materials, capable of emitting tuneable laser light, that covers all the range of wavelengths of the visible light, the principal object of the present patent. Furthermore, with the objective of improving the properties of those synthetic polymers usable as matrixes in the generation of laser light, we have developed a series of new polymers, preferably linear and cross linked, with the adequate structures and compositions for their adaptation in each case to different laser dyes, following different strategies.

One of the applications which demonstrates the versatility of the new laser system is that of the cleaning of pigmentary stains and, above all, tattoos, since the inks actually used in those show in their composition a varied number of pigments and dyes which cover all the scope of colors and shades. Therefore, their removal requires that for each color there should be used the wavelength that it absorbs, which implies the use of several lasers to remove a single tattoo.

Until now, the efficiency has been demonstrated in the cleaning of determined colors of a tattoo by means of the use of the fixed wavelengths emitted by the lasers of Nd:YAG and of Alejandrita. However, there are many other colors remaining that are difficult to remove, at the same time that satisfactory results only are achieved for merely some colors when indiscriminately high fluences are used. However, the use of high fluences involves serious limitations and problems as for the damages caused to the patient, with burnings and the risk of loss of the basal stratum of the epidermis, above other side effects, since the predominant mechanism of cleaning under those conditions is the photothermical one. Also, even under the most drastic conditions of irradiation, the long term treatments are not excluded, being usual treatments of between 6 and 12 sessions, with intervals between them of some 6 to 8 weeks, depending on the cases.

With regard to the actual knowledge, the most convenient and efficient way for the removal of a pigment stain or a tattoo should be the one based on the use of some irradiation conditions (wavelength, frequency and fluence) that selectively induce only the photochemical degradation of the pigments. As a consequence of this selective photodegradation of the pigments, small fragments and other products of their photolysis are formed which are removed from the skin through the lymphatic system, with the consequent bleaching of the tattoo, this way being avoided also the undesirable photothermolitic effects pointed out before.

By means of the use of the laser system which is described here, it has been achieved to remove satisfactorily, *in Vitro* and *in Vivo*, the pigments and dyes of a whole series of inks for tattoos of different colors and origins.

DESCRIPTION OF THE INVENTION

The present invention refers to a procedure to remove pigmentary stains and tattoos on the skin, characterized in that it comprises at least to apply in the area to be treated a laser light emitted by a solid state dye laser system which selectively emits at least one specific wavelength of the visible spectrum. In other words, this new laser can be tuned depending on whether it is desired at different concrete (discrete) values of wavelengths within the visible region of the spectrum, in terms of the active means used in the system for the regeneration of the laser light.

Preferably, the selected specific wavelength is comprised between 500 nm and 750 nm, both included.

In a preferred embodiment, the laser light is applied repetitively over an area to be treated, being used as an active means for the generation of said laser light a dye which is included in a solid matrix for each selected specific wavelength.

The selection of the different wavelengths at which the laser light shall be applied over the area with pigmentary stains or tattoos is determined by the color or the shade of the pigmentation. The more colors or shades are desired to be eliminated, the more different wavelengths will be necessary to achieve their total removal, one for each color or shade. For this reason, preferably before the application of the laser, the absorption spectrum of the pigmented area to be irradiated can be obtained, to select the specific wavelengths of the laser emission, necessary to remove all the pigmentations. The *modus operandi* consists, basically, in determining the wavelength at which it absorbs a determined color of the pigment stain or tattoo which is desired to be removed, this way to be able to choose an active means as emitter element at this wavelength. Given that the inks of tattoos absorb within the visible spectrum, sometimes it is sufficient to estimate visually its absorption range, even though it results more convenient to obtain its absorption spectrum by reflection, placing an optical fibre directly over the tattooed skin, this way to be able to choose the wavelength of laser emission that shows the maximum overlapping with the absorption of the inks of the tattoo.

After, it is proceeded to the irradiation of the pigment stain or tattoo, using a light conductive element that can be a device that is provided with the adequate reflection components, for example, an articulated optical arm or, preferably, an optical fibre.

In another preferred embodiment, and meeting the chromatic characteristics of the tattoo, its situation, the skin color of the patient and his sensitivity it can result convenient in some cases to cool the area of irradiation, for example by means of hydrogel applied in form of a fine film, or a cooled sapphire crystal, connected to the end of the fibre. In some cases, and to the judgment of the dermatologist, it can result advisable, even though not indispensable, to use also a local anaesthetic. After that, it is proceeded to irradiate the skin area to be treated, selecting the adequate parameters of laser light generation.

Preferably, said parameters are as follows:

- laser shot frequency excitation comprised between 1 Hz and 1 KHz, both limits included,
- output power comprised between 0.1 and 50 milijoules, both limits included, and
- fluence comprised between 0.025 and 2.5 J/cm2, both limits included.

Once the irradiation conditions are selected, the selected color or tonality area of that pigmentary stain or tattoo is swept with the laser beam of light, should establish the operator for the duration of the session. Given that under these conditions the photothermic processes are minimized, they can be utilized in more treatment times than when other non-optimized lasers are utilized. Thanks to this new invention, in the same session it can irradiate over other areas of the pigmentary stain or tattoo that have another different color tonality, prior change of the emission element (active medium) contained within the laser system that is adapted to the corresponding wavelength. In this manner, the sessions are appreciably shortened and the necessary times to remove a tattoo, as well as the time passed between session and session.

The object procedure of the present invention also is characterized because the laser emission can be generated in two ways:

- by transversal irradiation or pumping of the active medium, and
- by longitudinal irradiation or pumping of the active medium.

Likewise, the present invention is referred to an active medium for the generation and emission of a light beam in a laser radiation system utilized in the procedure described above for the removal of pigmentary stains and tattoos on the skin. Said active medium is characterized because it comprises at least a dye included in a solid matrix of at least a polymer, emitting each dye-matrix combination to a concrete wavelength within the visible spectrum. That is to say, the active medium will comprise many combinations of a dye with a solid matrix as wavelengths are selected for the laser application.

Since at present it does not yet exist a universal matrix capable of being utilized with any laser dye, it becomes essential selecting, adapting and optimizing a matrix for every selected dye. Preferably, the polymers that comprise the matrix or matrices of the present invention are selected from linear and cross-linked synthetic polymers. More preferably the polymers are selected from the ones obtained from the monomers of the group comprised by: methyl methacrylate, 2-hydroxyethyl methacrylate, pentaerythritol tetracrylate, trifluoromethyl methacrylate, pentaerythritol triacrylate, 2-hydroxyethyl acrylate and triethoxymethyl-silyl-propyl methacrylate, and combinations thereof. And even more preferably, each one of the solid matrices present a selected composition from: methyl polymetacrylate; hydroxyethyl methacrylate with methyl methacrylate copolymer, cross-linked with pentaerythritol tetracrylate; methyl methacrylate with trifluoromethyl methacrylate copolymer; copolymer de methyl methacrylate with pentaerythritol triacrylate; 2-hydroxyethyl polymethacrylate; and hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer.

Choosing dyes is carried out taking into account, for in addition to having some appropriate efficacies and stabilities, for emitting the wavelength. As it has been said above, in the present invention the selected dyes preferably cover among all the interval of 500 a 750 nm. Preferably, the utilized dyes belong to the perylene family, the sulforhodamines, the rhodamines, the LDS or a combination of them. More preferably, the utilized dyes are selected from Perylene 240, Perylene 300, Sulphorhodamine B, Rhodamine 640, LDS 698, LDS 722 and LDS 730.

The first criterion for selecting a laser matrix in the solid state is that said matrix presents no wavelength absorption of the absorption and emission of the selected dye, neither to the pumping or excitation. The second criterion, that is exclusive, is that of the laser dye solubility selected on en said matrix. For this, it can serve as a guide to verify de previous solubility of the dye in the monomer or monomers mixture, to the appropriate concentration to obtain a total absorption at the excitation or pumping wave length(s). Hereinafter, in the case of attaining the sought solubility, the solution of the dye in the monomer, or monomer mix, is treated with ultrasound, to favor to the greatest extent its solubility, and afterwards the resulting solution is ultrafiltrated, by utilizing 0.2 micron membrane, as a precaution for possible solid debris that could be present in the medium. Subsequently, proceed to the controlled polymerization of said solution, by choosing, in each case, the more adequate experimental conditions by following the procedures, methods and conditions described in our Spanish Patent 2 161 152 19, 2001. Once the polymeric matrixes that carry the laser dyes in the suitable ratios and concentrations have been obtained, is proceeded to its machining and polishing, following the usual procedures in the materials' machining, until reaching the desired geometric shape and dimensions, checking, visually and spectroscopically, if the selected dye is equally soluble in the final obtained polymer or copolymer.

Once these two requisites are satisfied, may be proceeded to the corresponding assessment of its laser properties and, when necessary, also of its photophysical and photochemical properties.

The main laser parameters that define a material usable as active medium in the generation of laser light are: its emission or yield efficiency; its photostability or life span at service and its laser emission tuneability or wavelength range. For the assessment as an active medium for the generation of laser irradiation of the new subject materials herein, there may be utilized different assemblies from the commonly employed in the known laser devices, although in the present case are recommended the two described in our Spanish Patent 2 161 152 19, 2001, as well as the cavities, pumping system and procedures detailed therein.

Among all the assessed matrixes combinations and dyes, only those with the best results covering the wavelength ranges of the visible were chosen. Preferably, the dye and solid matrix combinations utilized in the present invention for the generation of the laser light are the following:

- Perylene 240 included in a methyl polymethacrylate solid matrix, at a concentration comprised between 0.25 and 2.6 mM;
- Sulphorhodamine B included in a hydroxyethyl methacrylate with methyl methacrylate copolymer solid matrix in a 7 to 3 ratio by volume, cross-linked with pentaerythritol tetracrylate in a 10% ratio, at a concentration comprised between 0.5 and 1.5 mM;
- Perylene 300 included in a methyl methacrylate with trifluoromethyl methacrylate copolymer solid matrix in a 7 to 3 ratio by volume, at a concentration comprised between 0.15 and 1.6 mM;
- Rhodamine 640 included in a methyl methacrylate with pentaerythritol triacrylate copolymer solid matrix in a 9 to 1 ratio by volume, at a concentration comprised between 0.1 and 1.5 mM;
- LDS 698 included in a 2-hydroxyethyl polymethacrylate solid matrix, at a concentration comprised between 0.07 and 0.66 mM;
- LDS 722 included in a hydroxyethyl methacrylate with

triethoxymethyl-silyl-propyl methacrylate copolymer solid matrix in a 8 to 2 ratio by volume, at a concentration comprised between 0.05 and 0.55 mM; and

- LDS 730 included in a hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer solid matrix in a 7 to 3 ratio by volume, at a concentration comprised between 0.75 and 0.85 mM.

More preferably, the described dyes are diluted in their respective solid matrixes with the following molar concentrations:

- Perylene 240: 7.5x1
- Sulphorhodamine B: $6x10^{-4}$ M
- Perylene 300: $5x10^{-4}$ M;
- Rhodamine 640: $6x10^{-4}$ M;
- LDS 698: $4x10^{-4}$ M;
- LDS 722: $4x10^{-4}$ M; y
- LDS 730: 8x10-4 M.

In the accompanying Figure 1 the laser spectra of some of the new dye-solid matrix combinations are shown, where it may be observed the overlapping of the laser light emissions within the area of interest, and in the table 1 below are summarized the main laser parameters of the selected materials, transversely pumped at 532 nm.

TABLE 1

Laser dye and Polymeric matrix*	**Laser efficienc y (%)**	**λ emiss ion (nm)**	**Range of tuneability (nm)**	**Photostability after 100.000 pulses (%)**
a) Perylene 240 [$7.5x10^{-4}$ M] p(MMA)	40	579	568-598	37
b) Sulphorhodamine B [$6x10^{-4}$ M] cop(HEMA/MMA (7/3) + PETRA 9/1)	40	608	580-645	99
c) Perylene 300 [$5x10^{-4}$ M] cop(MMA/TFMA 7/3)	21	618	605-655	95

d) Rhodamine 640 [6x10^{-4} M] cop(HEMA/PETA 9/1)	36	640	620-660	79
e) LDS 698 [4x10^{-4} M] p(HEMA)	21	660	635-695	55
f) LDS 722 [4x10^{-4} M] cop(HEMA/TMSPMA 8/2)	23	674	650-720	67
g) LDS 730 [8x10^{-4} M] cop(HEMA/TMSPMA 7/3)	20	730	695-750	100

a) cop(HEMA/MMA 7/3 + PETRA 9/1 = hydroxyethyl methacrylate with methyl methacrylate copolymer in a 7 to 3 ratio by volume, cross-linked with pentaerythritol tetracrylate in a 10% ratio.

cop(MMA/TFMA 7/3) = methyl methacrylate with trifluoromethyl methacrylate copolymer in a 7 to 3 ratio by volume.

cop(HEMA/PETA 9/1) = methyl methacrylate with pentaerythritol triacrylate copolymer in a 9 to 1 ratio by volume.

b) p(HEMA) = 2-hydroxyethyl polymethacrylate.

cop(HEMA/TMSPMA 8/2 and 7/3) = hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer in an 8 to 2 and 7 to 3 ratios by volume.

Also, the present invention relates to a solid state dye laser irradiation system to remove pigmentary stains and tattoos on the skin according to the procedure described before. Said system is characterized in that it tunes wavelength discrete values comprised within the visible spectrum, for which it comprises at least the following devices:

- a cavity, wherein the active medium comprising at least one dye included in a solid matrix of at least one previously defined polymer is located,
- an excitation-pumping source of the active medium, and
- a wavelength tuner mechanism.

As the excitation or pumping light source, a light emitter may be preferably utilized selected between those with the following characteristics: coherent or non-coherent, ultraviolet or visible, monochromatic or polychromatic, and pulsed or continuous. More preferably, the excitation-pumping source comprises at least one visible, monochromatic, coherent and pulsed light emitter. In another preferred embodiment, a Nd:YAG laser is employed, being convenient to utilize its emission, frequency doubled, at 532 nm, with pumping repetition rates of between 1Hz and 10 KHz, and energies comprised between 0.1 and 50 millijules.

The active medium (laser emitter) is contained in the cavity with a geometric configuration suited to one of the two possible pumping types, transverse or longitudinal, aforementioned.

In transverse pumping, the preferred geometric configuration of each dye-matrix combination is, among all the possible ones, a cylinder of 1 cm height and a diameter of between 4 and 10 mm. Said cylinder must carry a flat side face, axis-parallel, of between 1 and 6 mm. Both the side face and the cylinder bases must be polished, at least, to optical quality.

Preferably, for the transverse focalization of the pumping beam on the flat face parallel to the axis of the matrix a pair of cylindrical lenses can be employed, in order to attain a rectangular irradiation spot of 10 mm by between 1 and 3 mm. In this type of cavities a standard polished aluminum mirror is utilized, as a reflecting element, locating it parallel, to about 2 cm of one of the faces of the cylinder, in order to minimize the dimensions of the cavity. This cavity is closed with a glass window, arranged parallel to the mirror at a distance of about 1 cm from the other face of the cylindrical sample. Thus, when the pumping over the dye-solid matrix combinations is transverse, the cavity should at least comprise:

- one pair of cylindrical lenses to focalize the excitation-pumping beam selectively over one of the dye and solid matrix combinations,
- a standard polished aluminum mirror as a reflecting element, and
- a glass window that closes the cavity, arranged parallel to the mirror.

In longitudinal pumping, the polymer matrix-dye preferred geometric configuration, among all possible, is a disk with a thickness higher than 1 mm and variable diameter, preferably higher than 10 mm. For the pumping or excitation of the sample a standard spherical lens and two dichroic mirrors may be employed, for the adjustment of this cavity to the diameter al diameter and divergence of the pumping beam.

The choice of the emission wavelength of this laser system, within the visible region of the spectrum, is accomplished by employment of the materials described as “active medium”, by selecting on each case the corresponding dye-matrix combination according to the desired wavelength. For this purpose, said selection may be carried out manually or automatically.

In the first option, in order to manually replace the polymer-dye emitter element by another, it's only necessary to arrange, inside the cavity, a support adapted to the geometric configuration of the dye-matrix emitter element, such that one piece may be readily substituted by another and that said support doesn't interfere with the light of the excitation or pumping beam, nor with the emission beam of the dye-matrix piece. For that matter, any attachment that accomplish this requisite may serve, as well as ensure the reproduction of the position when changing one piece by another, and therefore avoid the realignment after each changing or substitution operation of the emitter element. By way of example, in the case of utilizing a longitudinal pumping configuration, the simplest attachment of the sample may be a rod that traverses the disk through its geometric center.

For the mechanical swapping of said elements, different mechanisms and automatisms may be utilized between those currently available in the field of Optics. For this particular application, it would be preferably suitable a revolver or water wheel type device, housing each cylinder (transverse pumping) or disk (longitudinal pumping) in a circular manner around the central axis of the device, such as is shown in the Figure 2 for both configurations.

Definitively, the wavelength tuner mechanism consists of a support located inside the cavity, in the shape of a disk or rotating cylinder, that is traversed by a rod in its geometric center, and housing around said central axis of the disk or cylinder the dye-solid matrix combinations, in the manner of a revolver or water wheel type device.

In order to change a sample by another, the revolver or water wheel device only has to be rotated around its axis, until the new dye-matrix sample is located in the right position inside the cavity. The operation may be automatized by using a step motor acting as a microlocator, which is why its use and handling may be simply integrated, for example, inside the shooting frequency and output power control program of the laser.

In all that has been described above, the emitter element remains static during the excitation or pumping process. However, a substantial improvement in the duration of the laser system, subject of this patent, can be accomplished if the laser or the emitter element (active medium) is displaced during the excitation operation. Since in the static system the excitation and generation of the laser light takes place solely in a small volume element, the remainder of the total volume of the piece remaining completely unaltered, therefore, the remainder of the active material can be exploited by simple incorporation to the laser system of a dynamic mechanism that displaces the sample, in a controlled manner, during the operation of the system. Thus, in a preferred embodiment, the excitation-pumping source is displaced during the step of excitation, maintaining the active medium fixed. In another preferred embodiment, the active medium is displaced vertically or horizontally during the step of excitation-pumping, maintaining the source of excitation fixed.

In the case of the disk-shaped samples (longitudinal pumping), the displacement of the sample is carried out by simple turn of the axis supporting them, with the regulation of the turning speed proportionally with the pumping frequency or rate of the excitation laser. If it is considered necessary or convenient to exploit all the active surface of the disk, it may also be performed a scanning of the beam of the pumping laser by using a scanner, which would move the beam in, in a scanning displacement of the beam from the inside of the disk to the outside and vice versa, until upon the continued use of the laser the efficiency or yield of that piece would reach a minimum value.

Likewise, in the case of the cylindric-shaped samples (transverse pumping), a scanning may be performed with the beam of the pumping laser of the side face of the sample, that would remain static, or either the cylindric sample may be rotated on its central axis, at the suitable rate and proportional to the frequency of the excitation beam, which in this case would remain static.

DESCRIPTION OF THE FIGURES

Figure 1. Laser spectra of some of the dye-solid matrix combinations developed in the present invention that make up an active medium for the generation of laser light.

Figure 2. Design of a wavelength tuner for the laser system described in the present application, disk- or cylinder-shaped in the manner of a revolver or water wheel type device.

- 2.A: sample holder for longitudinal pumping.
- 2.B: sample holder for transverse pumping.

EMBODIMENT EXAMPLES

As representative examples, but not limiting, of the subject materials herein, following are described some examples concerning their procurement and properties, as well of those of the devices specifically developed for its utilization as solid-state dye lasers, and their assessment and application.

Example 1

Polymers and Copolymers Synthesis (Solid matrixes).

Among all the laser dyes currently known, are selected, in a fist step, all those of interest, in terms of their emission wavelength and of their efficiency or yield in the laser light emission.

Once it has been selected a specific laser dye, solutions thereof are prepared of between 0.5 and 2 mM in one monomer or in mixes of two or three of the chosen monomers in varying ratios. Once the solubility of said dye has been ensured in the mix of monomers, 20 ml of this solution are taken. The starter azobisisobutyronitrile (20 mg; 0.12 mmol) is added to each of these solutions, which in turn is solubilized by shaking and subsequent treatment in an ultrasound bath. Next, said solutions are microfiltrated, first with a 0.45 micron and followed by a 0.2 micron pore size membrane. The resulting solutions are poured over a polypropylene cylindric molds with an inner diameter comprised between 10 and 25 mm, inside of which the resulting solution deoxygenates by pure argon or nitrogen bubbling, by immersion in said solutions of a capillary during about ten minutes. The molds are closed and sealed under inert atmosphere and kept at 40°C during 48 hours. After this time has past, the initial solutions should be solidified, increasing then the temperature to 50°C, temperature at which the molds are maintained during at least another 24 hours. Next, in order to destroy the remainder of the starter that hadn't reacted, as well as to increase the degree of final conversion, the temperature is slowly increased again (5°C/day), until reaching 80°C, keeping it at this temperature during 2 more hours, to later on slowly chill the molds until reaching room temperature, in order to avoid the freezing of residual stresses that could affect the optic quality of the obtained material, proceeding then to unmolding the pieces.

Example 2

Assessment of the new polymers and copolymers as laser irradiation emitters.

The laser assessment of the obtained materials according to the procedure described in the earlier example, is carried out once conveniently machined and polished in the desired geometric shape, according to the design of the laser cavity intended to utilize. By way of example, for said laser assessment some of the devices described above may be employed, or the device described in the patent ES *19990001540,* shaping then the materials obtained herein in the form of cylinders of 1 cm height and 1 cm diameter, with a parallel to its axis cut, in order to obtain a side flat surface.

Among all the materials assessed, those which efficiency and stability values were the highest among all the assayed for each wavelength were chosen, at the same time looking for an overlapping between their emissions, within the spectral region of interest.

In Table 1 are presented some of the developed materials, as well as the corresponding values of their laser parameters: efficiency, emission wavelength, range of emission and photostability, obtained following the procedure described in the Example 1.

TABLE 1. Laser parameters of the selected materials

Laser dye and Polymeric matrix*	Laser efficiency (%)	λ emission (nm)	Range of tuneability (nm)	Photostability after 100.000 pulses (%)
Perylene 240 [$7.5x10^{-4}$ M] p(MMA)	40	579	568-598	37
Sulphorhodamine B [$6x10^{-4}$ M] cop(HEMA/MMA (7/3) + PETRA 9/1)	40	608	580-645	99
Perylene 300 [$5x10^{-4}$ M] cop(MMA/TFMA 7/3)	21	618	605-655	95
Rhodamine 640 [$6x10^{-4}$ M] cop(HEMA/PETA 9/1)	36	640	620-660	79
LDS 698 [$4x10^{-4}$ M] p(HEMA)	21	660	635-695	55

LDS 722 [4x10^{-4} M] cop(HEMA/TMSPMA 8/2)	23	674	650-720	67
LDS 730 [8x10^{-4} M] cop(HEMA/TMSPMA 7/3)	20	730	695-750	100

* Pumping conditions: transverse pumping at 532 nm, 10 Hz; energy: 5 mJ/pulse, during 100.000 pulses in the same position.

The efficiency, tuneability and photostability obtained results show the feasibility of utilization of these new materials as laser light emitters, object of the present patent of invention.

<u>Example 3</u>

Laser system with wavelength selector (or tuner)

Said laser system consists of the elements and devices described below.

As the source of excitation or pumping light, a Nd:YAG laser is utilized, with emission, frequency doubled, at 532 nm, pumping repetition rates of between 1Hz and 10 KHz, and energies comprised between 0.1 and 50 millijules.

As cavity, for transverse pumping, a configuration of the dye-solid matrix combinations is utilized consisting of a cylinder of 1 cm height and a diameter of between 4 and 10 mm. Said cylinder should carry a flat side face and of 10x4 mm. Both that side face and the cylinder bases must be polished to optic quality. For the transverse focalization of the pumping beam on the flat face parallel to the axis of the matrix one pair of cylindrical lenses was employed, that allow to obtain a irradiation area of 10 mm by between 1 and 3 mm. A standard polished aluminum mirror is utilized as a reflecting element, locating it parallel, to about 2 cm of one of the faces of the cylinder and a glass window, arranged parallel to the mirror at a distance of about 1 cm of the other face of the cylindric sample.

The choice of the emission wavelength of this laser system, within the visible region of the spectrum, is achieved by employing the materials described in the Table 1 of the Example 2, selecting in each case the corresponding dye-matrix combination according to the desired wavelength. For this purpose, said selection may be carried out in a manual or automatic way.

In order to manually replace the dye-matrix emitter element by another, it's only necessary to locate it inside the cavity, on a support adapted to its geometric configuration in the manner of a counter mould, such that the attachment and the reproduction of the position when changing one piece by another is ensured.

For the mechanical swapping of said elements a revolver or water wheel type device is utilized, wherein different dye-matrix cylinders are housed, as is shown in the Figure 2.

In order to change a sample by another, the revolver or water wheel device only has to be rotated around its axis, until the new dye-matrix sample is located in the right position inside the cavity. This operation may be automatized by using a step motor acting as a microlocator, which is why its use and handling may in turn be integrated, for example, inside the shooting frequency and output power control program of the laser.

With this device, the desired wavelength can be selected, according to the emissions of the available polymer-dye cylinders.

Example 4

***In Vitro* cleaning of the inks employed for tattoos.**

A hydrated collagen was chosen as a human skin mimetic medium, showing a similar consistency to that of the dermis when prepared at a concentration of 120 mg per water milliliter, locating over this layer a regenerated cellulose membrane of 2 micron of thickness which, in turn, mimics the epidermis. Inks for commercial tattoos from different sources that are added dispersed in water to the hydrated collagen are utilized, at a 100 mg of ink per milliliter of distilled water ratio. Thus, 238 mg of dry collagen are weighted for the preparation of a standard sample to which 1.64 ml of hot water are added dissolving the collagen and 0.35 ml of the tattoos ink suspension. The resulting solution is poured hot on a 35.5 mm diameter Petri dish; allow cooling down and placed inside a refrigerator to complete solidification. Next, its surface is covered with the hydrated cellulose membrane, not allowing air bubbles to be trapped between the both of them, being able to proceed then to the irradiation of the samples thus prepared.

According to the color of the tattoo ink employed, in order to accomplish total bleaching it is necessary to optimize the laser irradiation wavelength, the fluence and number of shots, for some fixed dimensions of the irradiation area.

Thus, when radiating a 2.6 x 3.4 mm surface of different colors with four wavelengths (448, 532, 599 and 1064 nm), the results have been:

- Yellow (Sun Yellow) 448 nm; 2.6 J/cm^2; 10+10 pulses.
- Orange (Light Orange) 532 nm; 0.6 J/cm^2; 5 pulses.
- Rose (Dusty Rose) 532 nm; 0.6 J/cm^2; 1 pulse.
- Rose (Monterrey) 532 nm; 0.9 J/cm^2; 1 pulse.
- Red (Dyn-O-Mite Red) 532 nm; 0.6 J/cm^2; 1 pulse.
- Red (Blood Red) 532 nm; 0.6 J/cm^2; 1 pulse.
- Red (Red Fire) 532 nm; 0.9 J/cm^2; 1 pulse.
- Red (Red Plum) 532 nm; 0.9 J/cm^2; 1 pulse.
- Brown (Russet Brown) 1064 nm; 0.54 J/cm^2; 3 pulses.
- Violet (Violet) 448 nm; 2.6 J/cm^2; 1x10 pulses.
- Blue (Bluejai) 599 nm; 2 J/cm^2; 1x3 pulses.
- Green (Irish Green) 448 nm; 2.6 J/cm^2; 10 pulses.
- Black (Midnite Black) 1064 nm; 0.3 J/cm^2; 1x5 pulses.

This results show that in order to the process of removing the tattoo may proceed exclusively by photolysis of the pigment-dye, such that besides being effective no adverse effects due to thermolysis are present, it is necessary to irradiate within the absorption range of the tattoo ink.

Example 5

Tattoos cleaning.

By utilizing the system and devices described in the previous Example 3, we proceeded to the cleaning of different tattoos.

In view of the amount of variables to be studied and assessed with regard to the profusion of existing commercial inks, the color and the shade of the skin, the age of potential patients and their tattoos, tattoo engraving procedure or technique, etc., it is extremely tedious the experimental performance of a complete *in Vivo* study on the assessment of the materials and the subject laser system of this Patent, for this application.

For this reason, by way of example, the results obtained by radiating, with the most suitable laser emission wavelength, an engraved two colors tattoo: rose and red, over a rabbit's shaved ear, which had been previously sacrificed for the food industry.

By employing an optic fiber the reflecting spectrum of the two colors can be obtained, proving that the absorption range is, for both colors, between 450 and 600 nm.

A Perylene 240/PMMA laser is chosen and start by radiating at very low fluence (0.6 J/cm^2). In the first session, only one shot per position was applied. The fluence may be increased to 0.8 J/cm^2, to therefore reduce the number of shots. The gradual disappearance of the tattoo color becomes evident from the first shot.

The process is completed until the total disappearance of the tattoo.

CLAIMS

1. Procedure to remove pigmentary stains and tattoos in the skin characterized in that comprises at least the application to the area to be treated of a laser light emitted by a solid state dye laser system, which selectively emits at least at a specific wavelength within the visible spectrum.

2. A procedure to remove pigmentary stains and tattoos in the skin according to claim 1, characterized in that the selected specific wavelength is comprised between 500 nm and 750 nm, both included.

3. A procedure to remove pigmentary stains and tattoos in the skin according to any one of claims 1 or 2, characterized in that the laser light is applied repeatedly over the area to be treated, a dye included in a solid matrix being utilized for each specific wavelength selected, as active medium for the generation of said laser light.

4. A procedure to remove pigmentary stains and tattoos in the skin according to any one of the preceding claims, characterized in that the laser light is generated according to the following parameters:

- shooting frequency of the excitation laser comprised between 1 Hz and 1 KHz, both included,
- output power comprised between 0.1 and 50 millijules, both included, and
- fluence comprised between 0.025 and 2.5 J/cm^{2}. both included.

5. A procedure to remove pigmentary stains and tattoos in the skin according to any one of the preceding claims, characterized in that further comprises some of the following steps, prior to the laser application:

a) obtaining the absorption spectrum of the pigmented area to be radiated, for selecting the specific laser emission wavelengths required to remove the pigmentations, and

b) refrigerating said pigmented area.

6. A procedure to remove pigmentary stains and tattoos in the skin according to claim 5, characterized in that step b) consists of locally anesthetize the area to be radiated.

7. A procedure to remove pigmentary stains and tattoos in the skin according to any one of the preceding claims, characterized in that the laser emission is generated by radiating or transverse pumping of the active medium.

8. A procedure to remove pigmentary stains and tattoos in the skin according to any one of the preceding claims, characterized in that the laser emission is generated by radiating or longitudinal pumping of the active medium.

9. Solid state dye laser irradiation system to remove pigmentary stains and tattoos in the skin according to the procedure described in any one of claims 1 to 8, characterized in that said system tunes wavelength discrete values comprised within the visible spectrum, and comprises at least the following devices:

- a cavity, wherein an active medium comprising at least one dye included in a solid matrix of at least one polymer is located,
- an excitation-pumping source of the active medium, and
- a wavelength tuner mechanism.

10. Laser irradiation system according to claim 9, characterized in that the excitation-pumping source comprises at least one light emitter possessing the following characteristics a), b), c) and d), each one of them being selected between the two given options:

a) ultraviolet and visible;
b) monochromatic and polychromatic;
c) coherent and non-coherent; and
d) continuous and pulsed.

11. Laser irradiation system according to claim 10, characterized in that the excitation-pumping source comprises at least one visible, monochromatic, coherent and pulsed light emitter.

12. Laser irradiation system according to any one of claims 9 to 11, characterized in that the excitation-pumping source is displaced during the step of excitation, maintaining the active medium fixed.

13. Laser irradiation system according to any one of claims 9 to 11, characterized in that the active medium is displaced vertically or horizontally during the step of excitation-pumping, maintaining the excitation source fixed.

14. Laser irradiation system according to any one of claims 9 to 13, characterized in that the cavity further comprises:

- one pair of cylindrical lenses to focalize the excitation-pumping beam selectively over one of the dye and solid matrix combinations,
- a standard polished aluminum mirror as a reflecting element, and
- a glass window that closes the cavity, arranged parallel to the mirror.

when the pumping over the dye-solid matrix combinations is transverse.

15. Laser irradiation system according to any one of claims 9 to 13, characterized in that the cavity further comprises:

. a standard spherical lens to focalize the excitation-pumping beam selectively over one of the dye and solid matrix combinations, and

· dos dicrhoic mirrors

when el pumping over the dye-solid matrix combinations is longitudinal.

16. Laser irradiation system according to any one of claims 9 to 15, characterized in that the wavelength tuning mechanism consists of a support located inside the cavity, in the shape of a disk or rotating cylinder, that is traversed by a rod in its geometric center, and housing around said central axis of the disk or cylinder the dye-solid matrix combinations, in the manner of a revolver or water wheel type device.

17. Active medium for the generation and emission of laser light in a laser irradiation system described in any one of claims 9 to 16, characterized in that said medium comprises at least a dye included in a solid matrix of at least one polymer, each dye-matrix combination emitting a specific wavelength within the visible spectrum.

18. Active medium according to claim 17, characterized in that the polymers comprising the solid matrix are selected between linear and cross-linked synthetic polymers.

19. Active medium according to any one of claims 17 or 18, characterized in that the polymers are selected between those obtained from the monomers of the group comprised of: methyl methacrylate, 2-hydroxyethyl methacrylate, pentaerythritol tetracrylate, trifluoromethyl methacrylate, pentaerythritol triacrylate, 2-hydroxyethyl acrylate and triethoxymethyl-silyl-propyl methacrylate, and combinations thereof.

20. Active medium according to claim 19, characterized in that each one of the solid matrixes presents a composition selected between: methyl polymethacrylate; hydroxyethyl methacrylate with methyl methacrylate copolymer, cross-linked with pentaerythritol tetracrylate; methyl methacrylate with trifluoromethyl methacrylate copolymer; methyl methacrylate with pentaerythritol triacrylate copolymer; 2-hydroxyethyl polymethacrylate; and hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer.

21. Active medium according to any one of claims 17 to 20, characterized in that the utilized dyes belong to the family of the perylenes, the sulphorhodamines, the rhodamines, the LDS or a combination thereof.

22. Active medium according to claim 21, characterized in that the utilized dyes are selected between Perylene 240, Perylene 300, Sulphorhodamine B, Rhodamine 640, LDS 698, LDS 722 and LDS 730.

23. Active medium according to any one of claims 17 to 22, characterized in that it comprises the following combinations:

- Perylene 240 included in a methyl methacrylate solid matrix, at a concentration comprised between 0.25 and 2.6 mM;
- Sulphorhodamine B included in a hydroxyethyl methacrylate with methyl methacrylate copolymer solid matrix at a 7 to 3 ratio by volume,

cross-linked with pentaerythritol tetracrylate at a 10% ratio, at a concentration comprised between 0.5 and 1.5 mM;
- Perylene 300 included in a methyl methacrylate with trifluoromethyl methacrylate copolymer solid matrix at a 7 to 3 ratio by volume, at a concentration comprised between 0.15 and 1.6 mM;
- Rhodamine 640 included in a methyl methacrylate with pentaerythritol triacrylate copolymer solid matrix at a 9 to 1 by volume, at a concentration comprised between 0.1 and 1.5 mM;
- LDS 698 included in a 2-hydroxyethyl polymethacrylate solid matrix, at a concentration comprised between 0.07 and 0.66 mM;
- LDS 722 included in a hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer solid matrix at a 8 to 2 ratio by volume, at a concentration comprised between 0.05 and 0.55 mM; and
- LDS 730 included in a hydroxyethyl methacrylate with triethoxymethyl-silyl-propyl methacrylate copolymer solid matrix at a 7 to 3 ratio by volume, at a concentration comprised between 0.75 and 0.85 mM.

24. Active medium according to claim 23, characterized in that the dyes are diluted in their respective solid matrixes with the following molar concentrations:
- Perylene 240: 7.5x10-4 M;
- Sulphorhodamine B: 6x10-4 M;
- Perylene 300: 5x10-4 M;
- Rhodamine 640: 6x10-4 M;
- LDS 698: 4x10-4 M;
- LDS 722: 4x10-4 M; and
- LDS 730: 8x10-4 M.

25. Active medium according to any one of claims 17 to 24, characterized in that each one of the combinations has the configuration of a 1 cm height cylinder and a diameter of between 4 and 10 mm, with a flat side face, parallel to its axis, of between 1 and 6 mm and polished to obtain optic quality, when said combinations are transversely pumped.

26. Active medium according to any one of claims 17 to 24, characterized in that each one of the selected combinations has the configuration of a disk with a thickness higher than 1 mm and variable diameter, when said combinations are longitudinally pumped.

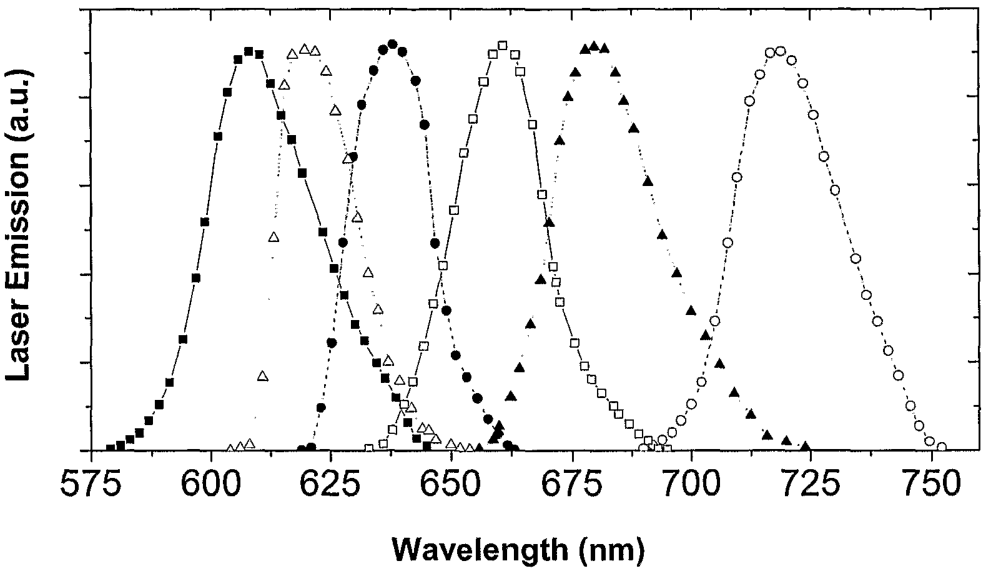
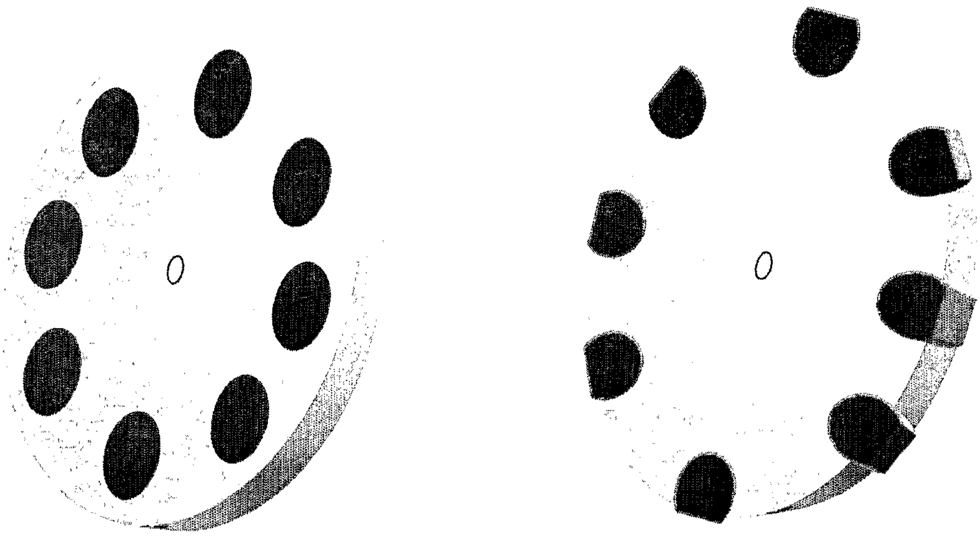


FIGURE 1



2.A. 2.B.

FIGURE 2