

(43) Date of A Publication **20.10.1999**

(21) Application No **9907503.8**

(22) Date of Filing **01.04.1999**

(30) Priority Data

(31) **09056493**

(32) **07.04.1998**

(33) **US**

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(51) INT CL⁶

B41N 1/14 , B41C 1/10 , B41N 1/00 , G03F 7/00

(52) UK CL (Edition Q)

G2C CHX CH6C4 CH6D2
B6C CHD C602 C636 C644

(56) Documents Cited

EP 0875395 A1 **EP 0769372 A1** **US 5893328 A**
US 5836249 A

(58) Field of Search

UK CL (Edition Q) **B6C CHD , G2C CHX**
INT CL⁶ **B41C , B41N**
ONLINE:EPODOC

(54) Abstract Title

Zirconia ceramic lithographic imaging members

(57) Long wearing lithographic imaging members (e.g. printing plates, cylinders, sleeves, tapes, Webs.) are prepared from a zirconia ceramic layer having thereon a hydrophilic, non-crosslinked water-insoluble surface layer composed of an inorganic oxide matrix. This surface layer is ablatable using imaging apparatus such as a laser, and the surface energy differential between the non-removed hydrophilic layer and the exposed underlying zirconia ceramic is desirable to provide lithographic printing with improved image sharpness.

The inorganic oxide matrix may comprise silica, silica-titania, silica-alumina or titanium-alumina or one or more colloids (sol-gels) of silicon, titanium and zirconium and have a surface energy of at least 50 dynes/cm.

The zirconia ceramic may be an alloy of zirconium oxide and a secondary oxide selected from MgO, CaO, Y₂O₃, Sc₂O₃, a rare earth oxide or a combination or any of these oxides.

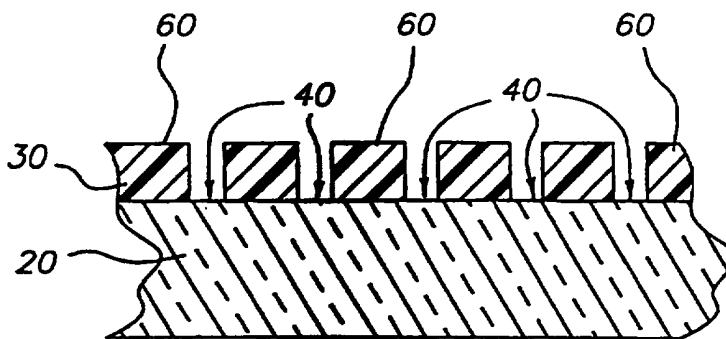


FIG. 2

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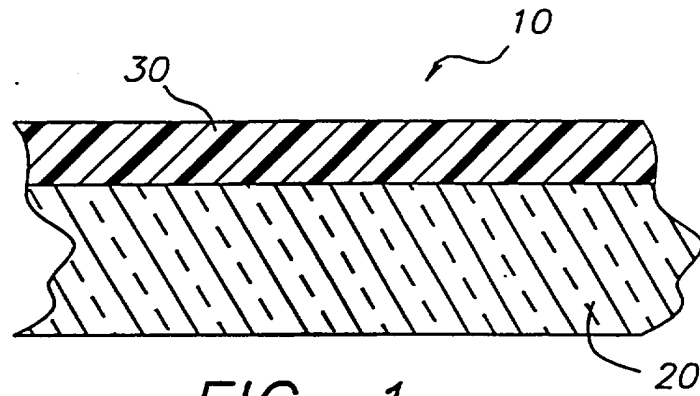


FIG. 1

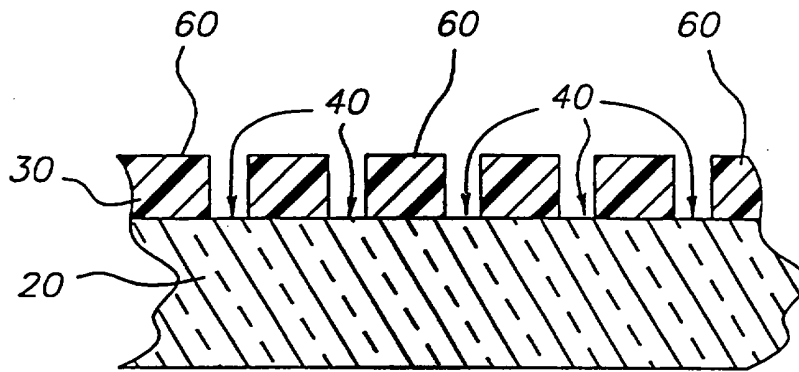


FIG. 2

ZIRCONIA CERAMIC IMAGING MEMBER WITH HYDROPHILIC SURFACE LAYER AND METHODS OF USE

This invention relates in general to lithography and in particular to
5 new and improved lithographic imaging members. More specifically, this invention
relates to novel imaging members having a zirconia ceramic layer and a hydrophilic
surface layer, and to a method of **imaging using** these imaging members.

The art of lithographic printing is based upon the immiscibility of oil
and water, wherein the oily **material or ink** is preferentially retained by the image
10 area and the water or fountain solution is preferentially retained by the non-image
area. When a suitably prepared **surface** is moistened with water and an ink is then
applied, the background or non-image area retains the water and repels the ink
while the image area accepts the **ink** and repels the water. The ink on the image
area is then transferred to the surface of a material upon which the image is to be
15 reproduced, such as paper, cloth and the like. Commonly the ink is transferred to
an intermediate material called the **blanket**, which in turn transfers the ink to the
surface of the material upon which the **image** is to be reproduced.

Aluminum has **been used** for many years as a support for
lithographic printing plates. In order to prepare the aluminum for such use, it is
20 typical to subject it to both a **graining process** and a subsequent anodizing process.
The graining process serves to **improve** the adhesion of the subsequently applied
radiation-sensitive coating and to **enhance** the water-receptive characteristics of the
background areas of the printing plate.

Lithographic **printing plates** of the type described hereinabove are
25 usually developed with a **developing solution** after being imagewise exposed. The
developing solution, which is **used to remove** the non-image areas of the imaging
layer and thereby reveal the **underlying** porous hydrophilic support, is typically an
aqueous alkaline solution and **frequently** includes a substantial amount of organic
solvent. The need to use and **dispose of** substantial quantities of alkaline
30 developing solution has long **been a matter** of considerable concern in the printing
art.

Efforts have been made for many years to manufacture a printing plate that does not require development with an alkaline developing solution.

Examples of the many references relating to such efforts include, among others:

US-A-3,506,779, US-A-3,549,733, US-A-3,574,657, US-A-3,793,033, US-A-
5 3,832,948, US-A-3,945,318, US-A-3,962,513, US-A-3,964,389, US-A-4,034,183,
US-A-4,054,094, US-A-4,081,572, US-A-4,334,006, US-A-4,693,958, US-A-
4,731,317, US-A-5,238,778, US-A-5,353,705, US-A-5,385,092, US-A-5,395,729,
EP-A-0 001 068, and EP-A-0 573 091.

Lithographic printing plates designed to eliminate the need for a
10 developing solution which have been proposed heretofore have suffered from one
or more disadvantages that have limited their usefulness. For example, they have
lacked a sufficient degree of discrimination between oleophilic image areas and
hydrophilic non-image areas with the result that image quality on printing is poor.
In addition, they have had oleophilic image areas which are not sufficiently durable
15 to permit long printing runs, they have had hydrophilic non-image areas that are
easily scratched and worn, or they have been unduly complex and costly by virtue
of the need to coat multiple layers on the support.

Ceramic printing members, including printing cylinders are known.
US-A-5,293,817, for example, describes porous ceramic printing cylinders having a
20 printing surface prepared from zirconium oxide, aluminum oxide, aluminum-
magnesium silicate, magnesium silicate or silicon carbide.

It has also been discovered that ceramic alloys of zirconium oxide
and a secondary oxide that is MgO, CaO, Y₂O₃, Sc₂O₃ or a rare earth oxide are
highly useful printing members, as described for example, in EP-A-0 769 372.

25 A zirconia ceramic having a stoichiometric composition is
hydrophilic in nature. Transforming the zirconia ceramic, such as during thermal
imaging, into a substoichiometric composition, renders the ceramic more
oleophilic. The total surface energy change from such transformations is 6 or 7
dynes/cm, which is sufficient to create a good image. However, image quality

could be improved substantially if the surface energy differential between the imaged and non-imaged areas could be made even larger.

While the zirconia ceramic imaging members described above are highly useful, and have a number of advantages over conventional materials, there is a need to provide ceramic imaging members having a greater surface energy differential between imaged and non-imaged areas on the printing surface.

This invention provides an imaging member comprising a zirconia ceramic layer, and characterized as having a hydrophilic, non-crosslinked, water-insoluble, surface layer composed of an inorganic oxide matrix, the hydrophilic surface layer having a surface energy of at least 50 dynes/cm.

This invention also provides a method of imaging comprising the steps of:

- A) providing the imaging member described above, and
- B) imagewise ablating the hydrophilic surface layer.

Further, this invention also provides a method of printing comprising the steps of:

- A) providing the imaging member described above,
- B) imagewise ablating the hydrophilic surface layer,
- C) contacting the imaged imaging member with a lithographic printing ink, and
- D) imagewise transferring the printing ink to a receiving material.

The imaging members of this invention have a number of advantages. For example, no chemical processing is required so that the effort, expense and environmental concerns associated with the use of aqueous alkaline developing solutions are avoided. Post-exposure baking or blanket exposure to ultraviolet or visible light sources, as are commonly employed with many lithographic printing plates, are not required. Imagewise exposure of the imaging member can be carried out directly, for example, with a focused laser beam that ablates the hydrophilic surface layer in an imagewise fashion, leaving exposed areas of zirconia ceramic, and non-exposed areas of hydrophilic surface layer. The

surface energy differential between those two surfaces is a desirable increase over conventional materials. In particular, this differential should be at least 8 dynes/cm.

Exposure with a laser beam enables the imaging member to be imaged directly from digital data, and used in printing, without the need for intermediate films and conventional time-consuming optical printing methods. Since no chemical processing, wiping, brushing, baking or treatment of any kind is required, it is feasible to expose the imaging member directly on the printing press by equipping the press with a laser exposing device and suitable means for controlling the position of the laser exposing device.

A still further advantage is that the imaging member is well adapted to function with conventional fountain solutions and/or conventional lithographic printing inks so that no novel or costly chemical compositions are required.

The zirconia ceramic underlayer utilized in this invention has many characteristics that render it especially beneficial for use in lithographic printing.

Thus, for example, it provides durability, abrasion-resistance, and long wearability. Because of the increased hydrophilicity in the non-imaged areas (i.e., the hydrophilic surface layer), discrimination between oleophilic imaged areas and hydrophilic non-imaged areas is excellent. The imaging member can be of several different forms (described below) and thus can be flexible, semi-rigid or rigid. Its use in imaging and printing is fast and easy to carry out, image resolution is very high and imaging is especially well suited to images that are electronically captured and digitally stored.

FIG. 1 is a partial cross-sectional view of an imaging member of this invention prior to imaging.

FIG. 2 is a partial cross-sectional view of an imaging member of this invention after imaging.

The imaging member of this invention comprises a zirconia (or alloy) layer composed predominantly of zirconia (or an alloy described below) of stoichiometric (ZrO_2) composition. The zirconia ceramic layer serves as the imaged areas since the hydrophilic surface layer is imagewise ablated. The imaged

areas then provide more oleophilic surfaces than the non-imaged areas and will therefore take a lithographic ink more readily.

The zirconia layer can be composed simply of zirconia oxide. Alternatively, the zirconia layer comprises a composite of zirconia and alumina (Al₂O₃). In such embodiments, the zirconia comprises at least 50% (by weight) of the ceramic. Preferably, the zirconia comprises from 50 to 99.9%, and more preferably from 70 to 90% (by weight) of the ceramic. The alumina within the composite is in the rhombohedral form or phase (this may be indexed as hexagonal by a crystallographer), and is known as α -alumina. Zirconia-alumina compositions can also be prepared using the zirconia alloys described below.

In a preferred embodiment, the zirconia ceramic is an alloy comprising a secondary oxide selected from the group consisting of MgO, CaO, Y₂O₃, Sc₂O₃, rare earth oxides (such as Ce₂O₃, Nd₂O₃ and Pr₂O₃), and combinations and mixtures of any of these secondary oxides. The secondary oxide can also be referred to as a dopant. The preferred dopant is Y₂O₃. The dopant provides high strength and enhanced fracture toughness.

The molar ratio of secondary oxide (dopant) to zirconium oxide preferably ranges from 0.1:99.9 to 25:75, and is more preferably from 0.5:99.5 to 5:95 when the dopant is yttria.

The zirconia used in any embodiment of this invention can be of any crystalline form or phase including the tetragonal, monoclinic and cubic crystalline forms, or mixtures of any two or more of such forms or phases. The tetragonal form is predominantly used because of its high fracture toughness especially in the alloys and composites including yttria as the secondary oxide.

The hydrophilic, non-crosslinkable, water-insoluble surface layer can be provided on the zirconia ceramic layer in a number of ways. Preferably, it is directly applied, but can also be applied to an intermediate layer that is also ablated during imaging.

In one embodiment, the hydrophilic surface layer can be composed of a matrix of one or more inorganic oxides, such as silica, titania, silica-titania,

silica-alumina, and titania-alumina matrices. These materials can be applied as dispersions and dried to form a water-insoluble layer, with or without a binder material that can be burned away after the dispersion is applied to the ceramic layer. For example, a thin layer of silica, or a silica-titania composite, can be applied by physical vapor deposition, chemical vapor deposition or thermal spray. Other techniques, such as dip, spray, knife or rod coating, can also be used.

Preferably, one or more binder materials are used to adhere or coalesce the oxide particles after coating and drying. These organic binder materials are not crosslinkable, but provide a physical bonding among the oxide particles. Such binder materials include, but are not limited to, polyvinyl alcohol, polyalkylene glycols (such as polyethylene glycols), polyacrylates and polymethacrylates. A preferred binder material is polyvinyl alcohol. The amount of binder used in such formulations can be at least 3 weight % of the total hydrophilic composition before it is dried.

In a preferred embodiment, the hydrophilic layer inorganic matrix is formed from one or more colloids of beryllium, magnesium, silicon, arsenic, indium, tin, antimony, tellurium, lead, titanium, bismuth or a transition metal oxide. Aluminum oxide is not useful for this purpose when used alone. Such colloids are often called "sol gels" or colloidal sols. Colloids of silicon, titanium and zirconium oxides are preferred, and a colloid of silicon or mixture of silicon and titanium are most preferred. Such colloids can be obtained from hydroxysilicates, hydroxytitanates and hydroxyzirconates. Methods for forming these colloids are described in US-A-2,244,325, US-A-2,574,902 and US-A-2,597,872. Stable dispersions of such materials can be purchased from various sources including DuPont Company. The hydrophilic layer is most effective when it contains a minimum amount of hydrophobic groups such as methyl or other alkyl groups. The hydrophilic layer preferably should contain less than 5% hydrocarbon groups by weight.

The hydrophilic layer can also include addenda such as surfactants, dyes, and colorants for coatability, visibility and improved light absorption.

This layer has a critical thickness so the energy levels required for ablation imaging are not too high. Thus, the dry thickness is from 0.05 to 1 μm , and preferably from 0.075 to 0.1 μm . This layer also has a surface energy of at least 50 dynes/cm, preferably at least 55 dynes/cm, and more preferably at least 60
5 dynes/cm.

Surface energy can be measured by conventional methods. One useful method involves the use of Fowkes Analysis. In this, the contact angles between a set of fluids and the clean surfaces of the materials being evaluated are measured. More specifically, the contact angles were measured on the bare
10 zirconia ceramic and the hydrophilic layer using a Rame-Hart contact angle goniometer. The test fluids used for these measurements were double deionized water for the polar part and diiodomethane (or methylene iodide) for the dispersive part of the total surface energy. The average static contact angle for each test fluid was measured by placing an approximately 7.5 μl drop of the fluid on the sample,
15 and using the goniometer when the fluid was at an equilibrium state (that is, when the fluid no longer advances along the surface).

The imaging members of this invention can be of any useful form including, but not limited to, printing plates, printing cylinders, printing sleeves, and printing tapes (including flexible printing webs). The imaging member can
20 include the zirconia ceramic and hydrophilic surface layers disposed on a suitable substrate material, often known as a support. Useful support materials include metals, polymeric films, glass and non-zirconia ceramics.

Printing plates can be of any useful size and shape (for example, square or rectangular). Hollow or solid steel or aluminum cores can be used as
25 substrates if desired. Such printing members can be prepared using methods described above for the printing plates, or fitted around another less expensive metal core. Printing tapes can be formed either on a rigid or semi-rigid substrate to form a composite with the zirconia ceramic and hydrophilic surface layers. In addition, the printing tapes of this invention, in the form of a continuous web,
30 enable a user to use different segments of the tape for different images. The tape

would therefore provide continuity within the "same printing job" even if the images differed. The user need not interrupt the work to change conventional printing plates in order to provide different printed images.

5 The zirconia alloys and composites useful herein, and methods of manufacturing are in more detail in US-A-5,290,332, US-A-5,336,282 and US-A-5,358,913. The density and porosity of the zirconia ceramic can be varied by adjusting their consolidating parameters, such as pressure and sintering temperature.

10 Thermal or plasma spray and chemical vapor deposition (CVD) and physical vapor deposition (PVD) can be carried out using conventional procedures, either in air or in an oxygen environment to produce hydrophilic layers on ceramic surfaces.

15 The imaging member of this invention may be formed using a sol-gel dispersion, and may also be subjected to a heating step after the hydrophilic surface layer is formed, and before imaging. This heating can be used to "burn away" the organic additives and solvents (including binders), and to otherwise densify the inorganic oxide matrix. Heating is generally at a temperature of at least 200 °C for a few minutes up to an hour.

20 The imaging members of this invention can be imaged by any suitable technique on any suitable equipment, such as a plate setter or printing press. In one embodiment, the essential requirement is imagewise exposure to radiation which is effective to ablate the hydrophilic surface layer, leaving the zirconia ceramic exposed in imaged areas. Thus, the imaging members can be imaged by exposure through a transparency or can be exposed from digital
25 information such as by the use of a laser beam. Preferably, the imaging members are directly laser written. The laser, equipped with a suitable control system, can be used to "write the image" or to "write the background."

30 For imaging, it is preferred to utilize a high-intensity laser beam with a power density at the printing surface of from 30×10^6 to 850×10^6 watts/cm² and more preferably from 75×10^6 to 425×10^6 watts/cm². However,

any suitable exposure to electromagnetic radiation of an appropriate wavelength can be used as long as ablation of the hydrophilic surface layer on the ceramic layer occurs.

An especially preferred laser for use in imaging the imaging member
 5 of this invention is an Nd:YAG laser that is Q-switched and optically pumped with a krypton arc lamp. The wavelength of such a laser is 1.064 μm .

The conditions of laser exposure are controlled to “ablate”, burn away or loosen a portion of the hydrophilic surface layer in the exposed regions. Thus, a pit is formed in the exposed regions from the removal of “ablated”
 10 hydrophilic surface layer. If the hydrophilic surface layer is very thin, ablation may also remove or melt part of the zirconia ceramic layer, and may render it even more oleophilic. The preferred laser imaging conditions for this method are as follows:
 Laser Power: Continuous wave **average** - 0.1 to 50 watts, preferably from 0.5 to 30 watts,
 15 Peak power (Q-switched) - 6,000 to 10^5 watts, preferably from 6,000 to 70,000 watts,
 Power density - 30×10^6 to $850 \times 10^6 \text{ W/cm}^2$, preferably from 75×10^6 to $425 \times 10^6 \text{ W/cm}^2$,
 Spot size in TEM₀₀ mode = 100 μm ,
 20 Current = 18 to 24 amperes, preferably from 19 to 24 amperes,
 Laser energy = 6×10^{-4} to $5.5 \times 10^{-3} \text{ J}$, preferably from 6×10^{-4} to $3 \times 10^{-3} \text{ J}$,
 Energy density = 5 to 65 J/cm^2 , preferably from 7 to 40 J/cm^2 ,
 Pulse Rate = 0.5 to 50 kHz, preferably from 1 to 30 kHz,
 Pulse Width = 50 to 300 nsec, preferably from 80 to 150 nsec,
 25 Scan Field = 11.5 x 11.5 cm,
 Scan Velocity = no more than 3 m/sec,
 Repeatability in pulse to pulse jitter = about 25% at high Q-switch rate (about 30 kHz), <10% at low Q-switch rate (about 1 kHz).

FIG. 1 shows an imaging member 10 of this invention comprising
 30 zirconia ceramic layer 20 and hydrophilic surface layer 30, prior to imaging.

In FIG. 2, the same imaging member is shown after imaging, and hydrophilic surface layer 30 has been removed in exposed (imaged) areas 40, leaving non-imaged areas 60.

The invention is further illustrated by the following examples of various useful printing members.

Example 1:

Colloidal sol-gel compositions containing either synthetized tetraethyl silicate or tetraisopropyl titanate were obtained from Petrarch Systems, Inc. (Bristol, Pennsylvania). These compositions contained 5 weight % solids. They were combined (20:80 titania to silica) with stirring at 40 °C for 30-45 minutes. The dispersion was cooled to room temperature, filtered and stored in a refrigerator until used.

Thin (about 0.050 to 0.075 micrometer thickness) coatings of the noted sol-gel mixture were made on zirconia ceramic substrates using a Headway spin coater at 2,000-5,000 rpm for 15 to 60 seconds. These substrates were composed of zirconia alloyed with 3 mol % yttria (prepared from powder obtained from Zirconia Sales of America, Atlanta, Georgia). The faster the coating speed, the thinner the coatings. The coated members were then heated in an air furnace at about 275 °C for 30-45 minutes.

Polar and dispersive surface energy measurements were made using a Rame-Hart, Inc. goniometer to measure the contact angles of water and methylene iodide of the coated hydrophilic layer. The hydrophilic surface layer having a mixture of titania and silica was determined to have a total surface energy of 64 dynes/cm.

Example 2:

Another imaging member of this invention was prepared similar to that described in Example 1 except solely a silica sol-gel was applied to the

zirconia ceramic surface. After heating, the total surface energy measurement of the hydrophilic surface layer was determined to be 52 dynes/cm.

Example 3 and Comparative Example 1:

5 The imaging members described in Examples 1 and 2 were
imagewise exposed to laser imaging at 1.06 μm wavelength using an Nd:YAG
laser under the conditions shown in Table I. A Comparative Example 1 imaging
member comprising an uncoated zirconia substrate was also exposed to the laser.
The resulting surface energies of the hydrophilic surface layer are also shown in
10 Table I below.

Before imaging, the bare zirconia ceramic of the Comparative
Example 1 imaging member had a total surface energy of 48 dynes/cm, and upon
imaging the total surface energy had changed to 41 dynes/cm. The results from
imaging are also shown in Table I. The surface energy differential between the
15 Example 2 non-imaged areas and the imaged areas was 11 dynes/cm, which is
desirably larger than the differential between non-imaged and imaged areas of
uncoated zirconia (7 dynes/cm). The differential in the imaged member of
Example 1 was even higher, 23 dynes/cm. It also appears that the imaging
current is critical, that is it must be above 18 amperes.

20

Comparative Example 2:

The imaging members described in Examples 1 and 2 hereinabove
were imagewise exposed to laser imaging at 1.06 μm wavelength using an
Nd:YAG laser under the condition shown in Table 1 below.

25

The surface energy of the silica sol-gel coated zirconia ceramic
had a surface energy of 52 dynes/cm, and upon irradiation at 15 Amp current and
0.1 watt laser power, it was not possible to ablate the thin sol-gel coating to
effectively image the zirconia substrate underneath.

Table I

MEMBER	PULSE RATE	CURRENT	SCAN VELOCITY	LASER POWER	SURFACE ENERGY	IMAGING RESULTS
Example 2	1 kHz	22 Amp	50 m/sec	2.2 watts	52 dynes/cm	Good image
Example 1	1 kHz	19 Amp	50 m/sec	1.0 watt	64 dynes/cm	Good image
Comparative Example 1	1 kHz	19 Amp	50 m/sec	1.0 watt	41 dynes/cm	Good image
Comparative Example 2	1 kHz	15 Amp	50 m/sec	0.1 watt	52 dynes/cm	No image

CLAIMS:

1. An imaging member comprising a zirconia ceramic layer, and characterized as having a hydrophilic, non-crosslinked, water-insoluble surface layer composed of an inorganic oxide matrix, the hydrophilic surface layer having a surface energy of at least 50 dynes/cm.
2. The imaging member as claimed in claim 1 wherein the inorganic oxide matrix comprises silica, silica-titania, silica-alumina or titania-alumina.
3. The imaging member as claimed in claim 2 wherein the organic oxide matrix further comprises an organic polymer binder.
4. The imaging member as claimed in any of claims 1 to 3 wherein the inorganic oxide matrix comprises a colloid of beryllium, magnesium, silicon, arsenic, indium, tin, antimony, tellurium, lead, titanium, bismuth or a transition metal oxide.
5. The imaging member as claimed in any of claims 1 to 4 wherein the hydrophilic surface layer has a surface energy of at least 55 dynes/cm.
6. The imaging member as claimed in any of claims 1 to 5 wherein the zirconia ceramic is composed of an alloy of zirconium oxide and a secondary oxide selected from the group consisting of MgO, CaO, Y₂O₃, Sc₂O₃, a rare earth oxide, and a combination of any of these oxides.
7. The imaging member as claimed in any of claims 1 to 5 wherein the zirconia ceramic is a zirconia-alumina composition comprising from 70 to 90%, by weight of zirconia.

8. The imaging member as claimed in any of claims 1 to 7 wherein the hydrophilic surface layer has a dry thickness of from 0.05 to 1 μm .

- 5 9. A method of imaging comprising the steps of:
- A) providing the imaging member of any of claims 1 to 8, and
 - B) imagewise ablating the hydrophilic surface layer.

10 10. The method as claimed in claim 9 wherein the image is provided on the hydrophilic surface layer by ablation using the following laser imaging conditions:

- an average power level of from 0.1 to 50 watts,
- a peak power of from 6,000 to 100,000 watts (in Q-switched mode),
- 15 current of from 18 to 24 amperes,
- a pulse rate of no more than 50 kHz,
- an average pulse width of from about 50 to 300 nsec, and
- a scan velocity of no more than 3 m/sec.

20 11. The method as claimed in claim 10 wherein laser imaging current is from 19 to 24 amperes.



Application No: GB 9907503.8
Claims searched: 1-11

Examiner: Carol Davies
Date of search: 12 August 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): G2C (CHX) B6C (CHD)

Int Cl (Ed.6): B41C; B41N

Other: ONLINE: EPODOC

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0875395 A1 (KODAK)	
A	EP 0769372 A1 (KODAK)	
A	US 5893328 (KODAK)	
A	US 5836249 (KODAK)	

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

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