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AEROGEL FINGERPRINT MEDIA

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AEROGEL FINGERPRINT MEDIA

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to fingerprinting. Particularly, the present invention relates to a novel fingerprint medium usable in the customary manner by sprinkling on latent prints, to novel fingerprint plates and to novel fingerprint coatings. More particularly, the present invention relates to a novel fingerprint medium and to fingerprint plates that provide a totally clean fingerprinting process, and to undetectable fingerprint coatings for use on secure documents and the like. Even more particularly, the present invention relates to a novel fingerprint medium, to fingerprint plates and to fingerprint coatings that use a new high-tech fingerprint powder composed of aerogels.

2. Description of the Prior Art

Various compositions and methods have heretofore been employed for developing or recording latent fingerprints and for recording fingerprints in the intelligence community and in law enforcement. The conventional procedure for developing a latent fingerprint involves applying to the surface having such fingerprint thereon a small amount of a finely powdered solid material until the outline of the fingerprint becomes visible and then carefully spreading the applied powder over the fingerprint in order to bring out its pattern. Various substances including powdered metals such as aluminum and bronze, dragon's blood powder, a

gray powder consisting of finely ground French chalk and mercury, and a black powder having a lampblack or charcoal base have been employed for this purpose. The conventional procedure for taking fingerprints for criminal investigations and for fingerprint processing for various government agency personnel records uses ink applied to the fingers. Ink is generally applied to each finger by rolling one's finger onto an ink pad then transferring that person's fingerprints to a white card by rolling the inked finger leaving an impression of one's fingerprint thereon.

However, the powder compositions heretofore employed have certain disadvantages. Of particular note, many of the prior art fingerprint powders are not sufficiently sensitive and do not provide the desired contrast to clearly bring out the fingerprint pattern so that hand and fingerprints thus obtained lack clear visibility. Further, some of the prior art fingerprint powders have an abrasive action which tends to streak and/or obliterate the latent fingerprint when such powder is applied to the surface containing such fingerprint. A disadvantage of the ink fingerprinting system is the need to roll the finger twice, once to coat the finger with ink and again to transfer the print to a print sheet. Further, the use of ink is messy requiring one to thoroughly wash the ink from the fingers so that ink stains are not inadvertently left on unwanted surfaces.

U.S. Patent No. 4,226,740 (1980, **Worsham et al.**) discloses an infra-red responsive fingerprint composition and method for manufacturing by sifting and mixing a minor proportion of finely divided carbon black and a major portion of infra-red responsive finely divided pigments containing milori blue, manganese dioxide, aluminum powder and mica. A small amount of gum arabic as binder is included to facilitate adhesion of the print powder to latent prints. On white surfaces, the fingerprint powder is black. On dark surfaces, the fingerprint powder is brightly reflective so that when lifted or transferred to white backing the color changes from brightly reflective to black.

U.S. Patent No. 4,176,205 (1979, **Molina**) discloses a fingerprint powder and method for developing latent fingerprints. The powder is comprised of a powder

carrier, especially a mixture of silica and talc, containing a coloring agent, preferably a fluorescent dye. The fingerprint powder can be applied by blowing the powder over the surface containing the latent fingerprints, or by brushing or pouring the powder on such surface, or by immersion thereof in such powder.

Therefore, what is needed is a fingerprint medium that provides for a one-step, clean print processing. What is further needed is a fingerprint medium that has high sensitivity for detecting, developing and transferring fingerprints. What is still further needed is a fingerprint medium that provides for inkless fingerprinting. What is yet further needed is a fingerprint medium that can be used as a security coating on documents by governmental agencies and private businesses.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a fingerprint medium for a one-step, clean print processing. It is a further object of the present invention to provide a fingerprint medium that has high sensitivity for detecting, developing and transferring fingerprints. It still a further object of the present invention to provide a fingerprint medium that can be used as a security coating on documents by governmental agencies and private businesses for detecting unauthorized handling of secured documents.

The present invention achieves those and other objectives by providing a fingerprint medium made from aerogels. Aerogels are made up of small amorphous silica grains bound together in long branched strings. The branched strings form a three-dimensional network with air-filled pores in the 100 Angstrom region. Aerogels are a class of low density solid foams characterized by an open cell structure composed of particles typically less than 10 nanometers in diameter and pore sizes in the range of about 4 to about 500 nanometers in diameter. It is the structure that makes the aerogel such unique material. Considering the density and basic structure of glass as a base, aerogel is a uniquely porous substance that can have porosities greater than 99.9%. The micro-structure of the aerogel resembles a

three-dimensional network of interconnected beads of about 10 to about 100 Angstrom in size, with pore diameters formed by the bead structure of about 50 to about 500 Angstrom. The porosity is the mechanism used to design aerogels of various densities. While the density can vary, the material maintains many of the basic properties of glass.

Aerogels can be chemically designed with different combinations of metal oxides processed to the gel with trapped reactive particles, or coated after processing with the desired chemicals or metal. This versatility allows aerogels to be designed to be catalytic, reactive, or adsorptive.

An important engineering feature of aerogel materials is that they can be obtained as powders, films or monoliths of varying size. Silica aerogels typically have surface areas ranging from 800 to 1100 m^2/g. When metal oxides are incorporated into the silica structure, somewhat lower, but still impressive surface areas are obtained ranging from 300 to 800 m^2/g. The extraordinarily high surface areas ensure that the active adsorbent or catalytic sites are exposed. As mentioned previously, aerogels are made with a range of densities. Silica aerogel can be made with a density as low as 0.003 g/cm^3 (on the same order of density as air) up to full density glass of 2.2 g/cm^3.

The process used to make an aerogel is to form a semi-solid gel from a solution, called a sol-gel process. The sol-gel process is the name given to any number of processes that have a solution or "sol" which undergoes a solution-to-gelation (sol-gel) transition. The transition is the point where the solution becomes rigid, i.e. a porous mass or alcogel. Silica gels may be prepared from the sol-gel polymerization of silicon alkoxides. The resulting gel has some solvent as a liquid within its pores. A supercritical extraction method that eliminates surface tension forces that would collapse the solid by converting the liquid to a vapor is employed to dry the alcogel. Particularly, hydrolysis occurs when the tetraethoxy silane (TEOS) or tetramethoxy silane (TMOS) and water are mixed in a mutual solvent, ethanol (ETOH) or methanol (MEOH) respectively. The hydrolysis, or in some cases

polycondensation, reactions are initiated throughout the matrix at numerous sites within the TMOS or TEOS and water solution as mixing occurs. Both hydrolysis and condensation may occur by acid or base catalyzed bimolecular nucleophilic substitution reactions.

Sol-gel technology allows the incorporation of virtually any elements as oxides into the framework of the aerogel structure. For example, transition metal ions such as vanadium (a well known catalyst) may be placed molecularly into the framework of a silica aerogel structure. Thus, the metal may be placed on an atomic basis into a three-dimensional structure with the potential for product shape selectivity similar to that of zeolites such as ZSM-5, the Mobil catalyst that converts methanol selectively to gasoline products. An advantage of aerogel chemistry over others is that two or more elements can be combined to create the desired catalytic or adsorption properties desired.

A range of metal oxide-matrix aerogels have been prepared as transparent, homogeneous, monolithic solid materials. Silica, tantala, zirconia and mixtures of metal oxides have all been used as the matrix material, while the metals include the early transition metals such as Titanium, Vanadium, Yttrium, Zirconium, Niobium, Tantalum and Tungsten, plus the lanthanides Lanthanum and Samarium.

The two-phase system consists of solid silica (SiO_2), or a silicon/metal mix, and solvent filled pores. The density of the resulting aerogel can be varied by the amount of solvent (ETOH or MEOH) used in the original solution, or the amount of solvent filling the pores of the alcogel. In a silicon/metal mix, the metals can be bonded in the silica matrix or dispersed throughout the silica matrix with no chemical bonding. If the metals are not bound in the silica matrix, they must remain suspended in the solution until gelation occurs. Fluorescent materials may also be added to the aerogel matrix. This feature would be useful in applications where a coating of aerogel film is provided on envelopes containing secure documents or coated on the secure documents directly. One method would be to dip coat the aerogel film onto the envelopes or documents. Another method would be to usa a

very fine powder form of the aerogel coated onto the envelopes or documents. Both types of coatings would go undetected by unauthorized personnel because of the aerogel's transparent characteristics.

As made, aerogels are sensitive to water. Aerogels react with water to partially return to the starting reactants. The result of this is that the material may become soft, opaque and brittle. Because of aerogels affinity to water and oil and the ability to incorporate various chemical species or combinations of various chemical species within the aerogel matrix which may have specific or preferred adsorption characteristics, aerogels are very useful as fingerprint media.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows a slightly magnified photograph of a fingerprint impression in the fingerprint medium of the present invention.

FIGURE 2 shows a fingerprint captured on an fingerprint medium of the present invention where iodine vapor was used to highlight the fingerprint.

FIGURE 3 shows an enlargment of a fingerprint impression in the fingerprint medium of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The above objects can be accomplished according to the present invention and an efficient, sensitive fingerprint medium and a rapid, economical and clean method for detecting and recording fingerprints employing aerogel powders and films is provided.

During the development of aerogels for various other applications, it was found that an aerogel's affinity for water and oil and wax-like residues which are present on human skin and deposited by fingerprints or hands can be detected or recorded and their pattern sharply revealed by the use of the above-noted fingerprint

medium. It is particularly desirable that the fingerprint medium of the present invention have good adherence to even a small amount of oily or waxy fingerprint residues. It has been found for this purpose that silica gels and silica/metal gels, cumulatively called aerogels, are eminently suited for this purpose.

The micro-structure of the aerogel resembles a three-dimensional network of interconnected beads of about 10 to about 100 Angstroms in size, with pore diameters formed by the bead structure of about 50 to about 500 Angstroms. Silica aerogels typically have surface areas ranging from about 800 to about 1100 m^2/g. When metal oxides are incorporated into the silica structure, somewhat lower, but still impressive surface areas are obtained ranging from about 300 to about 800 m^2/g. The extraordinarily high surface areas ensure that the active adsorbent or catalytic sites are exposed.

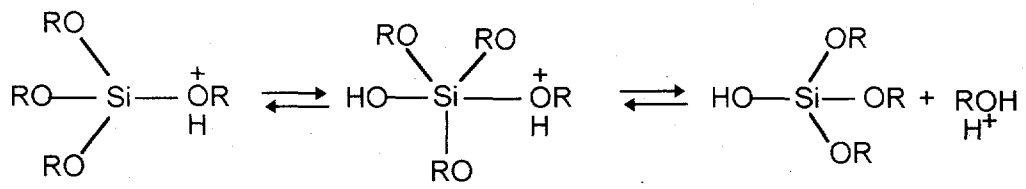
As mentioned above, the process used to make an aerogel is to form a semi-solid gel from a solution. Silica gels may be prepared from the sol-gel polymerization of silicon alkoxides. The resulting gel has some solvent as a liquid within its pores. A supercritical extraction method that eliminates surface tension forces that would collapse the solid by converting the liquid to a vapor is employed to dry the alcogel. Particularly, hydrolysis occurs when the tetraethyl silicate (TEOS) or tetramethyl silicate (TMOS) and water are mixed in a mutual solvent, ethanol (ETOH) or methanol (MEOH) respectively.

To reduce the number of intermediates existing as a result of partial hydrolysis, such as Si-OH groups or silanols, a limited amount of water is used in the initial solution. Silicic acid would be formed if complete hydrolysis of the $Si(OC_2H_5)_4$ to $Si(OH)_4$ occurred. It appears that either two silanols condense, or a silanol forms an oxygen bridge with a methoxy group to form Si-O-Si. A more complex mechanism exists for metal compounds bonded to the silicon throughout the alcogel's matrix. The hydrolysis, or in some cases polycondensation, reactions are initiated throughout the matrix at numerous sites within the TMOS (or TEOS) and water solution as mixing occurs. Both hydrolysis and condensation may occur by acid-

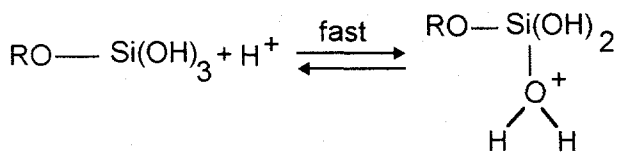
catalyzed or base-catalyzed bimolecular nucleophilic substitution reactions. The mechanisms are outlined below.

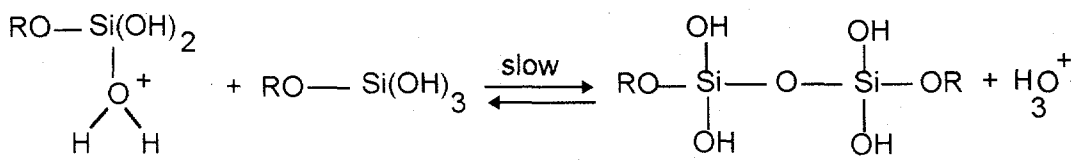
Mechanisms:

Acid-Catalyzed Hydrolysis

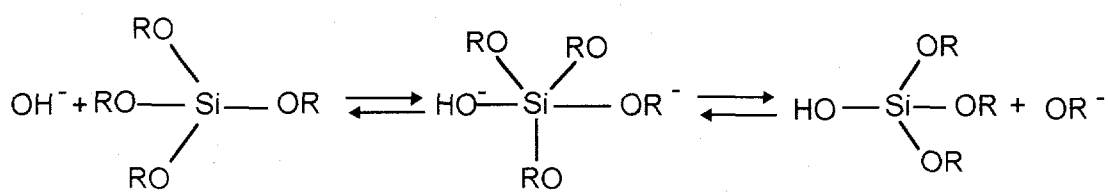


Acid-Catalyzed Condensation

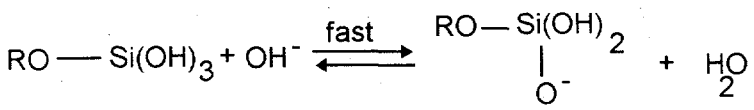


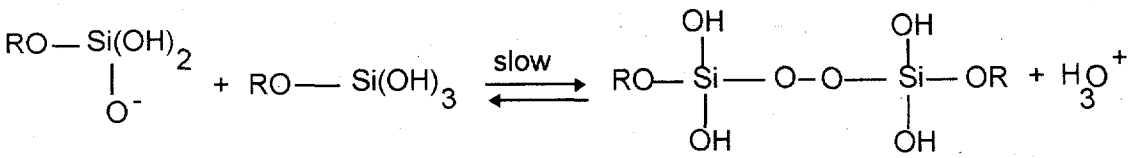


Base-Catalyzed Hydrolysis



Base-Catalyzed Condensation





The acid-catalyzed mechanisms are preceded by rapid deprotonation of the -OR or -OH substituents bonded to the silicone (Si). Under basic conditions, hydroxyl or silanolate anions attack Si directly. Some metal nitrates or combinations of metal nitrates, prevent the use of a basic catalyst due to the immediate formation of precipitates in the solution. To prevent this, an acid catalyst is used. The acidic solution helps keep the metal nitrate in suspension. Generally, this seems to increase the time to gelation. Slow hydrolysis is a symptom of low pH due to the formation of linear molecules that occasionally cross-link, with molecule chains ultimately entangling. When the molecular chains entangle, additional branches are created and gelation occurs. Under basic conditions, faster hydrolysis occurs due to the rapid formation of branched clusters that gel when the clusters link with each other.

A number of metals have been successfully incorporated into the aerogel matrix. Copper, cobalt, vanadium phthalocyanine, nickel, nickel and sodium palladium, platinum IV, iron, iron-cobalt-moly, cupric nitrate, cupric nitrate-chromium-moly, tetraamine platinum II chloride, cobalt-silver, ninhydrin, ceric nitrate-silver, ferric nitrate, tungsten-zinc, moly-platinum IV, platinum II, niobium-barium,

manganese-vanadium, silver-copper, nickel-rubidium, cadmium-nickel-niobium, silver fluoride, mercuric chloride, mercuric chloride-zirconyl nitrate, erbium-yttrium, erbium-yttrium-alumina, ferric nitrate-cobalt nitrate, neodynium-silver praseodymium-chromium, yttrium-ferric chloride-cobalt, chromium III-moly, and palladium sponge.

The aerogels of the preferred embodiment are prepared by hydrolysis of methyl orthosilicate in a methanol solution in an automated polaron (available from Fission Instruments). The critical point drying apparatus is a purely mechanical assembly. With the exception of the glass viewing window, pressure seals and gauges, it is constructed entirely of metal parts. The valving system does not require the constant adjustments that other polarons require. Pressure ranges from about 800 to about 1500 psi. Once the sol-gel transition occurs, the gel is placed in the polaron and the MEOH is exchanged with liquid CO_2. Alcohol evacuation is carried out by exchanging the methanol for liquid carbon dioxide (CO_2), and bleeding the methanol off through a vent port. CO_2 evacuation is carried out by heating the CO_2 to slightly higher than its critical temperature and venting the gas off slowly. By eliminating the liquid-gas interface, the basic integrity of the solid is maintained. By heating the gel until the critical temperature is reached, the liquid is converted to gas in a continuous fashion without two phases being simultaneously present at any time in the pores. The texture of such a solid is therefore not subject to any surface tension forces. After the supercritical extraction, the aerogel is either used in plate form or crushed or ground into small spherical pieces similar to activated charcoal granules. This is done to expose the maximum amount of available surface area for use as a fingerprint powder. The aerogel's affinity for water and oil and, in the case where carefully selected adsorption chemicals are incorporated, other chemical species makes it ideal as a fingerprint medium for obtaining latent fingerprints or for recording one's fingerprints for security reasons and the like.

Aerogels are made with a range of densities. Silica aerogel can be made with a density as low as 0.003 g/cm^3 through the use of the two-step process described above, up to full density glass of 2.2 g/cm^3. The metal oxide-silica aerogels have

typically been made with densities of 0.22 g/cm^3, while pure metal oxide aerogels such as tantala, have been made with densities from 0.1 to 0.7 g/cm^3.

The following example illustrates a preferred composition of the present invention for use as a fingerprint medium:

EXAMPLE 1

To make a 100 mg/cc density aerogel which is considered a mid-range density aerogel, weigh 15.2 grams of tetramethoxy silane and 16 grams of methanol into a beaker, beaker A. In a second beaker, beaker B, add 5 grams of water, 16 grams of methanol and 50 microliters of concentrated ammonium hydroxide as a catalyst. Add the contents of beaker B into beaker A, stir the contents of beaker A and let stand. The mixture will gel within 1 to 8 hours. The gel is then placed into a polaron (previously described). Liquid CO2 is added to the polaron so that the gel undergoes a CO2-methanol exchange. The CO_2-methanol exchange is carried out under pressure and at elevated temperature, preferably about 800 psi and in the range of about 20°C to about 100°C. The CO_2 and methanol are bled from the polaron to form the "dry" aerogel. To create aerogel plates, the polaron is bled very slowly so as not to collapse the aerogel structure. The resultant aerogel, whether in plate form or crushed to a fine powder, is hydrophilic and has a high affinity for oil and water making it a very good fingerprint medium. Fig. 1 shows a fingerprint on a plate form of the present invention made according to the above example. Fig. 2 shows the fingerprint on the fingerprint medium enhanced by the use of iodine vapor. Fig. 3 shows an enlarged view of Fig. 1 showing the detail of a print imposed on the plate form of the present invention made according to the above example.

The powder form of the present invention can be used to develop latent fingerprints. The prints can be enhanced by using an alternate light source manufactured by Omnichrome, Chino, CA 91710 (Model No. Spectrum 9000). The light source has the ability to provide various wavelengths of light selectable for giving the best definition to the latent prints. Iodine vapor can also be used to enhance a latent print by exposing the aerogel fingerprint to the vapor. Various

phosphorescent and fluorescent compounds may be added to the aerogel which makes latent prints even easier to see. In one mixture, fluorescene was added to the aerogel mixture before gelation in a concentration of about 1%.

The present invention may also be made in both low density and high density versions. The density of the aerogel varies inversely to the concentration of methanol used. The same holds true for aerogels prepared using tetraethoxy silane and ethanol. As one increases the amount of methanol used, the density decreases. Conversely, as the amount of methanol used decreases, the density increases.

For an ultra low density aerogel, one would use the following recipe: 189 grams of TMOS, 102 grams of MEOH, 49 grams of water and 7 drops of concentrated HCl as a catalyst. An ultra low density aerogel would be useful as a security coating on secure documents. Because ultra low density aerogel particles are so fine, it is practically impossible to completely wash off all the aerogel from one's hand. By using a black light, it would be obvious if an unauthorized person handled secured documents. The residual aerogel on the hands and clothing would fluoresce when exposed to the black light.

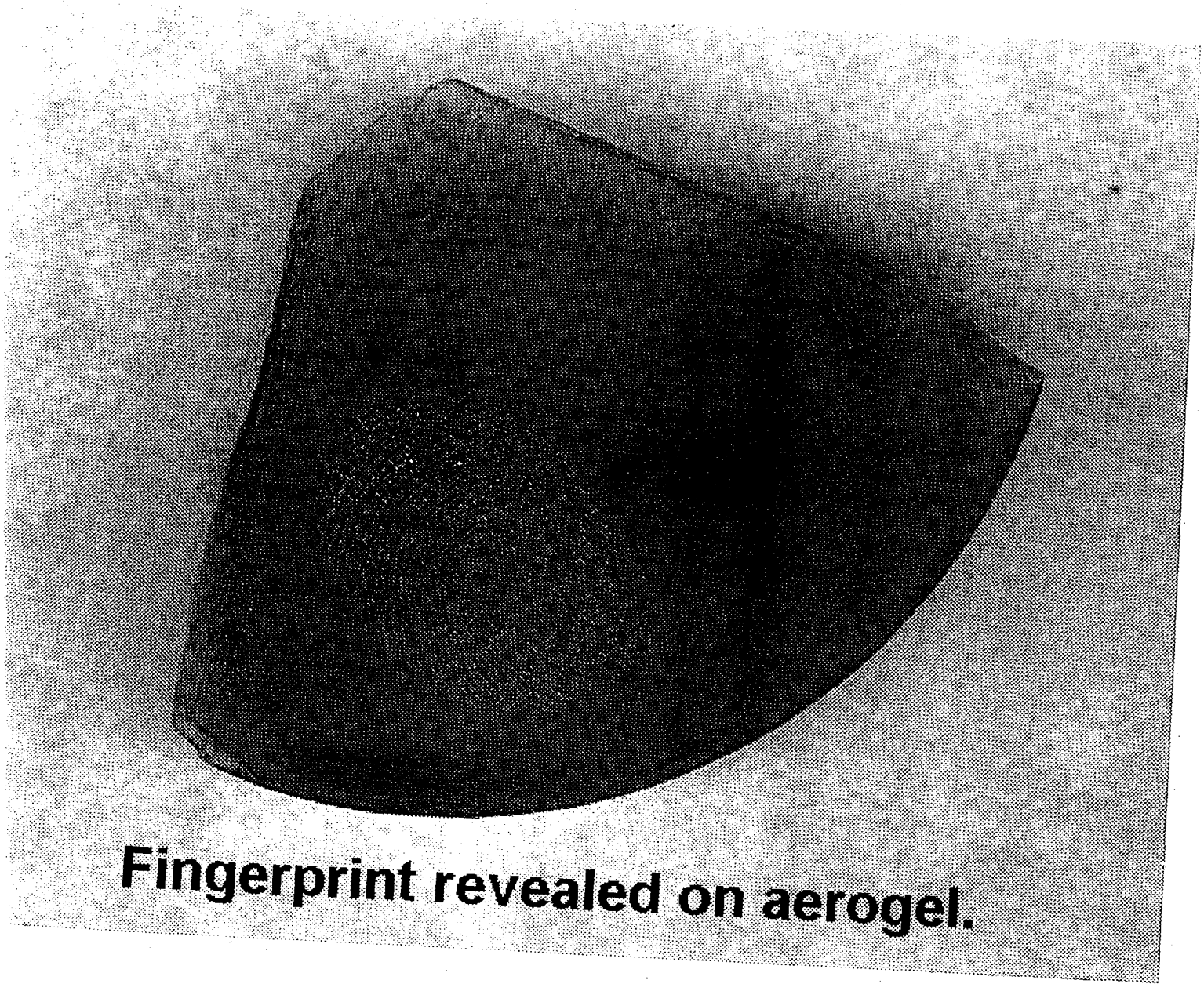
Particularly, the lanthanides incorporated in a aerogel/metal matrix are very good for creating highly fluorescent aerogels. As previously discussed various metal and metal oxide aerogels have been tested with similar success. When compared to currently used fingerprint powder which contains carbon black, the fingerprint medium of the present invention has the added benefit that it is approximately 1,000 times cleaner to use. That is, when a crime scene is dusted for fingerprints, the whitish appearance of the aerogel makes clean up afterwards easier and any residual aerogel much less visible due to its transparent characteristic than the carbon black of conventional fingerprint powders.

Although the preferred embodiments of the present invention have been described herein, the above descriptions are merely illustrative. Further modification of the invention herein disclosed will occur to those skilled in the respective arts and

all such modifications are deemed to be within the scope of the invention as defined by the appended claims.

ABSTRACT

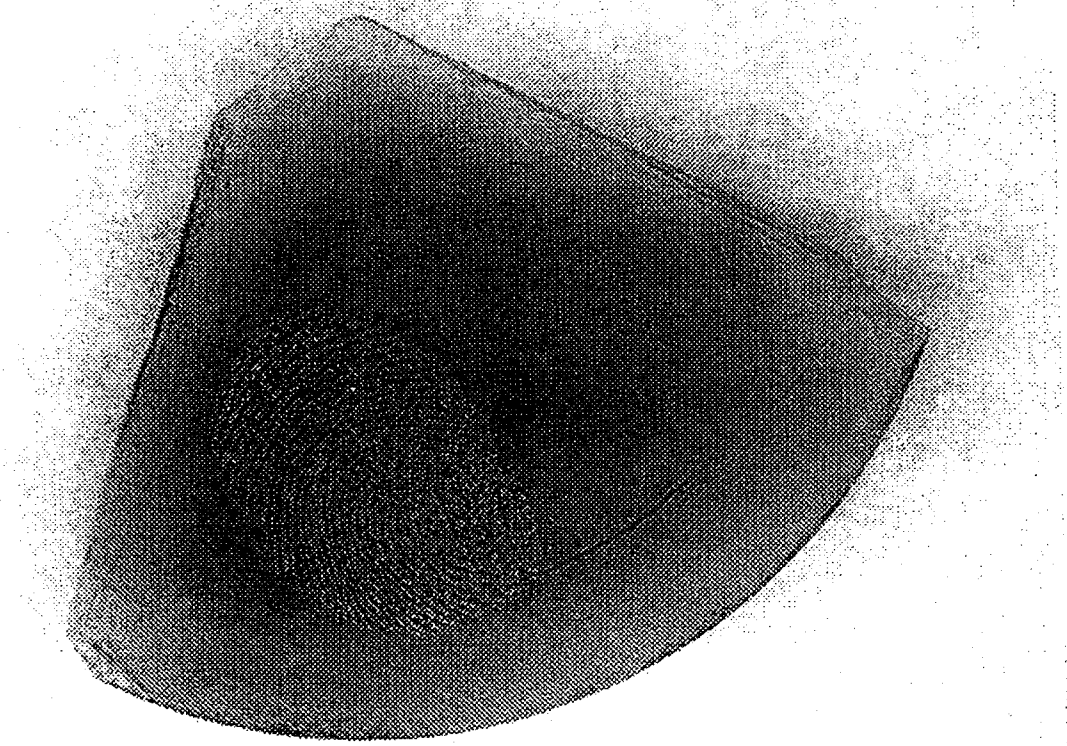
A fingerprint medium which is made of an aerogel having a predetermined density. The fingerprint medium may have a midrange density for forming plates or may be crushed forming a powder. The fingerprint medium may further include at least one of a metal and metal oxide to enhance characteristics desirable in a fingerprint medium.



Fingerprint revealed on aerogel.

Fig 1

Aerogel captures fingerprint



Iodine vapor highlights fingerprint

Fig 2

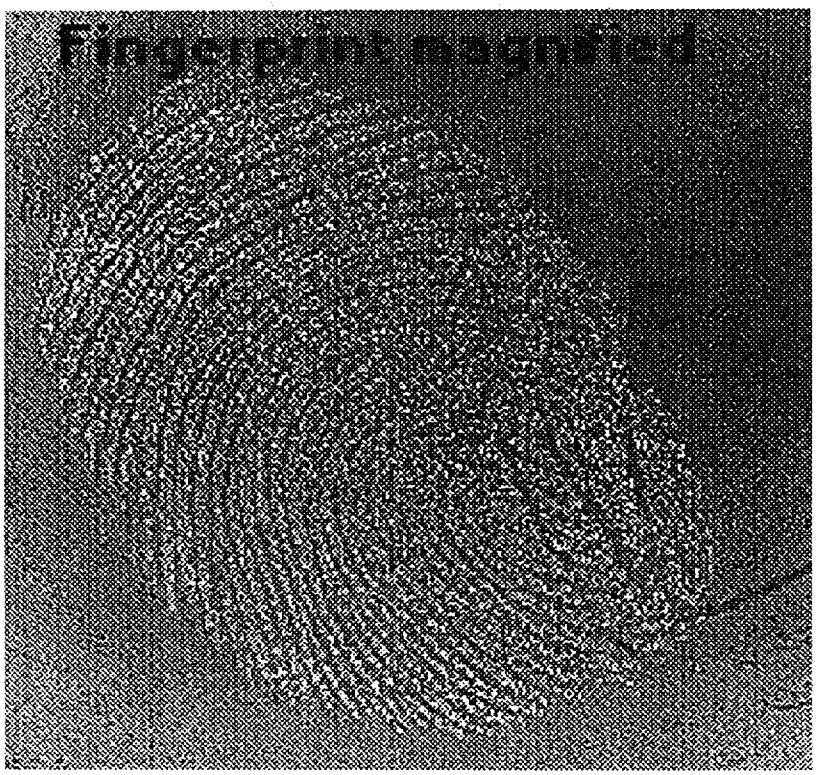


Fig. 3