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(54) **Pearlescent lamp.**

(57) A pearlescent lamp comprising a hollow glass envelope enclosing a source of electric light has its interior surface coated an iridescent optical interference film over which is disposed a layer of particulate titanium oxide, wherein both the iridescent film and titanium oxide layer have been formed in-situ inside the lamp envelope as a reaction product of gaseous $TiCl_4$ and H_2O. The iridescent film is first formed on the interior envelope surface and then an electrostatic potential is applied to the envelope which changes the reaction product to particulate titanium oxide which deposits on the interference film.

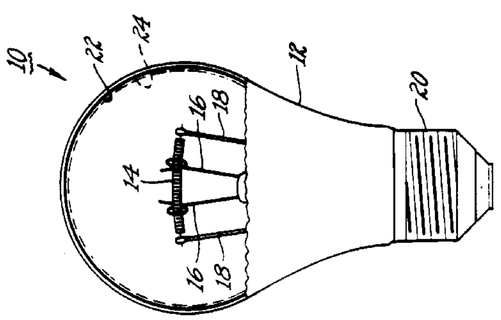

Fig. 1

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BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a vitreous article having a pearlescent coating. More particularly, this invention relates to an electric lamp having a pearlescent coating on the interior surface of the glass envelope to give the lamp a pearlescent appearance and to a process for producing the coating which comprises an iridescent film formed on the glass surface with a layer of titanium dioxide particles formed in-situ disposed adjacent the interference film.

Background of the Disclosure

Conventional incandescent lamps having a generally pear-shaped or round configuration comprising a sealed glass envelope with a metal screw base enclosing a filament within are known in the art as A-line and G-type lamps which consumers regard as ordinary electric bulbs. Most of these types of incandescent lamps are produced with the interior glass surface being etched or frosted and/or coated with a coating of a silica, alumina or titania powder inside to reduce or eliminate the filament image and provide more uniform illustration as is disclosed, for example, in U.S. Patent 4,042,747 and 4,441,087. These lamps are also available with clear glass envelopes and in various colors for use as decorative lamps and also as bug lamps. Attempts have been made in the past to coat the interior envelope or bulb wall with a particulate, light-scattering metal oxide powder coating formed in-situ inside the envelope. However, these methods have not met with commercial success. The light-scattering or diffusing particulate coatings are now electrostatically applied to the interior envelope surface using an electrostatic deposition process such as that disclosed in U.S. 4,081,709. One type of decorative incandescent lamp employs a single-layer titanium oxide optical interference film formed in-situ on the inner wall surface of the lamp envelope which gives the lamp envelope an iridescent appearance. The iridescent film is a reaction product of titanium tetrachloride and water vapor. Lamps of this type are manufactured and sold by GE as Auradescent lamps. Although the interference film produces an iridescent appearance when applied to a clear glass envelope, it is light transparent and therefore the filament is visible during operation of the lamp. It would be an improvement to the art if such lamps could also have a light-scattering coating to diffuse the filament image, provide more uniform illumination and provide additional decorative effects. Conventional light-scattering particulate coatings mentioned above have been found to destroy the iridescent effect when applied over the interference film inside the lamp envelope.

SUMMARY OF THE INVENTION

It has now been discovered that particulate titanium oxide formed by reacting a mixture of $TiCl_4$ and H_2O in-situ inside the lamp envelope and under the influence of an electrostatic potential provides a layer of particulate titanium oxide over the iridescent optical interference film which provides a lamp envelope having a white pearlescent appearance. This titanium oxide layer also diffuses the light source image and provides more uniform illumination without eliminating the iridescent effect of the optical interference film. Thus, in one embodiment the invention relates to a vitreous, light-transmissive article such as a lamp envelope and lamp having a pearlescent appearance. In another embodiment the invention relates to a process for forming particulate titanium oxide on an electrically nonconductive article which comprises reacting a gaseous mixture of $TiCl_4$ and H_2O in-situ in the vicinity of the article and under the influence of an electrostatic potential applied to the article, and also to an article produced by this process.

In one embodiment of fabricating a pearlescent lamp envelope according to this invention, an iridescent optical interference film is formed in-situ on the interior surface of the lamp envelope by reacting a gaseous mixture of $TiCl_4$ and H_2O inside the envelope, followed by applying an electrostatic potential to said envelope with said gaseous mixture present inside the lamp envelope. When the electrostatic potential is applied to the envelope, the reaction product of the gaseous $TiCl_4$ and H_2O mixture changes to a white titanium oxide powder which forms in-situ and is conveyed to the wall of the lamp envelope where it deposits as a layer on top of the iridescent film to give the lamp envelope a pearlescent appearance. Thus, the invention broadly relates to a product and a process for making the product wherein the product is a pearlescent article comprising a light transparent, vitreous body having two sides with at least a portion of one side coated with a coating having a pearlescent appearance, wherein said coating comprises an optical interference film on which is disposed a layer of titanium oxide particles.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 schematically illustrates a typical incandescent lamp having a pearlescent coating of the invention.

Figure 2 schematically illustrates a clear glass lamp envelope being coated with a pearlescent coating of the invention.

Figure 3 is a flow diagram of a process used in coating the interior of a glass lamp envelope with the pearlescent coating of the invention.

DETAILED DESCRIPTION

Turning to Figure 1, a conventional type of incandescent lamp 10 well known and old to those skilled in the art and to the average consumer is depicted as having vitreous, clear glass envelope 12 enclosing within filament 14 electrically connected to and supported on each end by leads 18 which extend through the seal of the lamp (not shown) and are attached by means not shown to the standard metal screw base 20. Additional support for filament 14, if necessary, is provided by additional support wires 16. The interior surface of envelope 12 is coated with an iridescent-appearing thin optical interference film 22 according to the invention over which is disposed a layer 24 of particulate titanium oxide powder formed and applied in-situ inside the envelope according to the process of the invention. The combination of thin film 22 and layer 24 provides the lamp with a pearlescent appearance according to the invention. Turning to Figure 2, which schematically illustrates a clear glass lamp envelope 12 being coated with a pearlescent coating according to the invention, envelope 12 is placed over reagent nozzles 26 and 28 by any suitable means (not shown). The glass envelope is preheated to a temperature of about 185°C. Reagent nozzles 26 and 28 supply air containing water vapor (H_2O) and gaseous titanium tetrachloride ($TiCl_4$), respectively, and, as shown in Figure 2, nozzle 26 which supplies moist air is inserted into envelope 12 slightly higher than nozzle 28 which supplies the air containing the $TiCl_4$ vapor. Power supply 32 provides a high voltage electrostatic potential typically of 26-33 kv. Lamp envelope 12 can be negative and the reagent supply tubes to 26 and 28 can be made positive, but from a manufacturing point of view it is simpler to make lamp envelope 12 positive and the reagent supply tubes 26 and 28 negative. In the laboratory, power supply 32 supplied a 30 kv positive potential to lamp envelope 12 and reagent supply tubes 26 and 28 were both grounded. In applying the pearlescent coating of the invention to the interior surface of a glass lamp envelope 12 in the laboratory, a clear glass envelope was first heated to a temperature of 185°C and placed over nozzles 26 and 28. Room temperature air containing H_2O vapor was passed through nozzle 26 into the interior 30 of the glass envelope 12 while, at the same time, room temperature air containing $TiCl_4$ vapor was passed through nozzle 28 into the interior of the lamp envelope. Nozzles 26 and 28 were fabricated from stainless steel tubing having an outside diameter of one-quarter of an inch. The flow rate of the H_2O vapor and $TiCl_4$ vapor-containing streams passing through nozzles 26 and 28 was 11 cubic feet per hour (cfh) and 16 cfh, respectively. These two streams mixed inside the lamp envelope to form a gaseous mixture of $TiCl_4$ and H_2O in air which reacted to form an iridescent-appearing optical interference film 22 on the inside surface of the hot lamp envelope. During this time, the 30 kv positive potential was not applied to the lamp envelope. That is, the iridescent-appearing optical interference film is formed on the inner wall of the hot envelope in the absence of any electrostatic potential. Further, the envelope must be hot or the optical interference film will not form. In general, if the reagent supplies being passed through nozzles 26 and 28 are at ambient room temperature, the lamp envelope should be at a temperature ranging between 150-220°C. If the temperature of the lamp envelope is outside this range under these conditions, then the iridescent film does not form and instead the reaction product, which is titanium oxide, forms a white, blotchy coating on the interior surface of the lamp envelope. The lamp envelope can be heated to higher temperatures, provided the reagent streams are heated to a temperature higher than ambient room temperature before being passed into the interior of the lamp envelope. As the iridescent-appearing optical interference film is being formed inside the lamp envelope (which generally takes around ten seconds), the hot lamp envelope is cooling down. Further, the lamp envelope itself does not have a uniform wall thickness due to manufacturing processes. This combination of cooling and differential wall thickness results in different temperatures at different portions of the lamp envelope at the same instant of time during the reaction of the reagents inside the cooling envelope, which results in a film of different thicknesses forming on the interior surface of the lamp envelope. This differential thickness of the optical interference film is what provides the iridescent or rainbow effect which manifests itself in a number of different colors.

The thickness of the interference film 22 will range between about 4000-7000 Å to give the various colored effects. The film itself is a titanium oxide and most probably titanium dioxide. At a thickness of between 4000-4500 the color will appear violet, whereas around 7000 Å the color will be red, with other colors of the spectrum in between these thickness ranges. If the coating is too thin many of the colors will be missing and if it is too thick it will be hazy to white with no iridescence. It should be noted that the iridescent coating can also be applied to the outside surface of the lamp envelope using the process of the invention, but forming the film inside the lamp envelope to deposit it on the interior surface of the envelope protects it from handling and oxidative degradation. It should be further noted that at the range of thicknesses of the film between 4000 to 7000 Å, the iridescent coating is light transparent. Thus, a clear glass envelope having just the iridescent coating applied to the interior surface will be light transparent as well as exhibiting a display of iridescent colors.

Immediately after the thin optical interference film of titanium oxide was formed on the interior surface of the lamp envelope, a 30 kv positive potential was applied to the outer surface of the lamp envelope as shown in Figure 2, with reagent nozzles 26 and 28 being grounded. This was done while the reagent flow was continuing. The reaction product, formed in-situ inside the lamp envelope as the result of the mixing of the $TiCl_4$ and H_2O-containing air streams under the influence of the applied electrostatic potential, changed to particulate titanium oxide particles which appeared as a white fume or smoke. This particulate titanium oxide product deposited over the just-formed optical interference film 22 as a thin layer of white, loose particles of titanium oxide (probably titanium dioxide). The thickness of the so-formed white, particulate titanium dioxide layer was about 3 to 10 thousandths of an inch. This gave the lamp envelope (and lamps made from such lamp envelopes) a whitish, pearlescent appearance. The pearlescent coating was translucent. It is interesting to note that attempts were made to achieve the same whitish, pearlescent appearance by applying pre-formed titania, alumina and silica and clay powders to the inside of lamp envelopes having an iridescent film applied by the process of the invention, but these did not produce a pearlescent appearance. Instead, the iridescent appearance was destroyed for reasons not fully understood. While not wishing to be held to any particular theory, it is believed that the looseness and morphology of the titania particles formed in-situ in the interior of the lamp envelope by reactions of the $TiCl_4$ and H_2O under the action of the electrostatic potential may have something to do with the pearlescent appearance achieved. Thus, the pearlescent coating according to the invention consists of an iridescent-appearing optical interference film over which is applied a layer of particulate titanium oxide formed in-situ inside the lamp envelope.

The stoichiometric reaction product of $TiCl_4$ and H_2O is TiO_2 and 4HCl. Accordingly, HCl was formed as a by-product of the reaction process and suitable arrangements must be made for collecting and disposing of it due to its toxicity and corrosive nature.

Figure 3 illustrates a schematic flow diagram of the process used to form a pearlescent coating on lamp envelopes according to the invention. Turning to Figure 3, air above atmospheric pressure is fed from a source (not shown) from line 40 through pressure regulator 42 and particulate filter 44 and from thence to dryer 46. It is important that the air be dry because of the reactivity of $TiCl_4$ with H_2O. From dryer 46 the dry air is passed through regulator 48 which brings it down to about atmospheric pressure and from there through line 50 to manifold 52. A portion of the air from manifold 52 is fed by line 54 through flow rater 56 and solenoid valve 58 to contacter 60 where it is mixed with water. In this particular case, 60 was a 1000 ml flask about three-quarters full of water with the dry air being fed to the bottom and then bubbling up through the water to produce moist air which is then passed via line 62 to mixer 64. At the same time, another portion of dry air is fed from manifold 52 through line 66, flow rater 68 and line 70 into mixer 64. The mixers are simple venturi mixers and merely insure that the moist air being delivered to nozzle 26 through line 72 contains about 63% of the moist air from line 62. Concomitantly, another portion of dry air is fed from manifold 52 through flow rater 86 and solenoid valve 88 to contacter 90 wherein it is contacted with liquid $TiCl_4$ in order to produce a $TiCl_4$-containing air stream 92 which, in turn, is fed to mixer 80. Mixer 80 is also a venturi type mixer. As with the moist air scheme, another portion of dry air is passed from manifold 52 through line 74, flow rater 76 and line 78 into mixer 80 wherein it mixes with the $TiCl_4$-containing air from line 92 and passed via line 82 to nozzle 28 whereby it is fed into the interior of lamp envelope 12. The air passing through nozzle 28 into lamp envelope 12 contains about 75% $TiCl_4$. As with mixer 60, mixer 90 is a 1000 ml flask about three-quarters full of liquid $TiCl_4$ wherein the dry air is passed into the bottom of the flask and bubbles through the liquid $TiCl_4$ to the surface thereof and then exits as air containing $TiCl_4$ vapor.

The foregoing is intended to be illustrative, but non-limiting with respect to the practice of the invention and the products produced thereof as those skilled in the art will appreciate. Thus, the optical interference film 22 could be formed from other materials and in other ways such as is known to those skilled in the art and could be either on the inside or outside surface of the lamp envelope. Further, the article being coated need not be a lamp envelope. It is essential, however, that the layer of particulate titanium oxide necessary for forming the pearlescent-appearing coating of the invention be formed in-situ inside or outside the lamp or other article being coated and under the influence of an electrostatic field and not coated by pre-formed titanium oxide powder.

Claims

1. An article having a pearlescent appearance which comprises a light-transmissive, vitreous article having a surface coated on at least a portion thereof with a pearlescent coating, wherein said coating comprises an optical interference film on which is disposed a layer of particulate titanium oxide formed as a reaction product of $TiCl_4$ and H_2O under the influence of an electrostatic potential.

2. An article according to claim 2 wherein said optical interference film is a reaction product of $TiCl_4$ and H_2O.

3. An article according to claim 3 wherein said opt-

ical interference film ranges between 4000 to 7000 Å thick.

4. An article according to claim 1 or 3 wherein said electrostatic potential is applied to said article during formation of said particulate titanium oxide.

5. A lamp comprising a hollow, light-transmissive, vitreous envelope enclosing a light source within wherein at least a portion of the interior surface of said envelope is coated with an optical interference film on said interior surface of said envelope and with a layer of particulate titanium oxide formed as a reaction product of $TiCl_4$ and H_2O under the influence of an electrostatic potential disposed adjacent said optical interference film.

6. A lamp according to claim 5 wherein said particulate titanium oxide is formed in-situ inside said lamp envelope.

7. A lamp or article according to claim 1 or 6 wherein said optical interference film provides an iridescent appearance.

8. A lamp according to claim 7 which has a pearlescent appearance.

9. A lamp according to claim 8 wherein said optical interference film is formed in-situ inside said lamp envelope as a reaction product of $TiCl_4$ and H_2O.

10. A lamp according to claim 9 wherein said optical interference film is between 4000 to 7000 Å thick and wherein said particulate titanium oxide layer ranges from 3 to 10 thousandths of an inch in thickness.

11. A process for applying a pearlescent coating to at least a portion of the interior surface of a vitreous, light-transmissive article, said process comprising contacting a gaseous mixture of titanium tetrachloride and water with said interior surface of said article, with said surface being at a temperature between 150-220°C and said contacting being for a time sufficient to form an iridescent-appearing optical interference film comprising a reaction product of said titanium tetrachloride and water adjacent said surface and formed in-situ inside said article and, after said optical interference film has been formed, applying an electrostatic potential to said article to form, in-situ adjacent said film as a reaction product of said gaseous $TiCl_4$ and H_2O, a layer of white, particulate titanium oxide.

12. A process or article according to claim 1, 4 or 11 wherein said article is a vitreous lamp envelope.

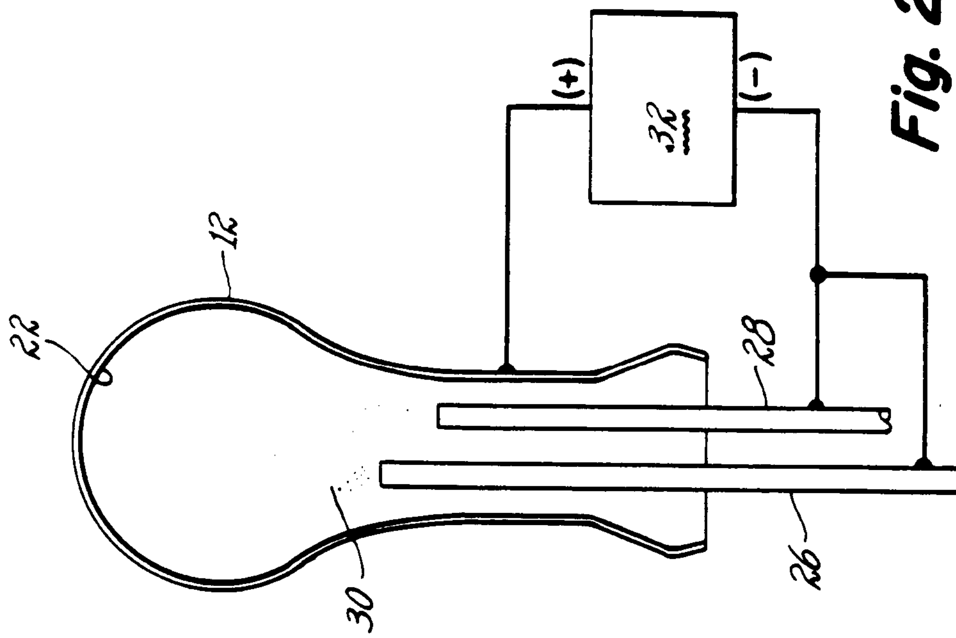

Fig. 2

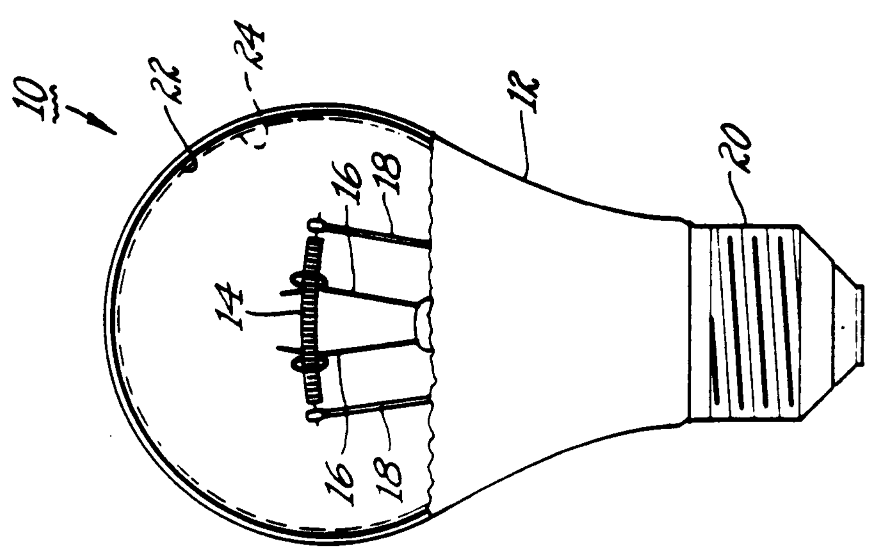

Fig. 1

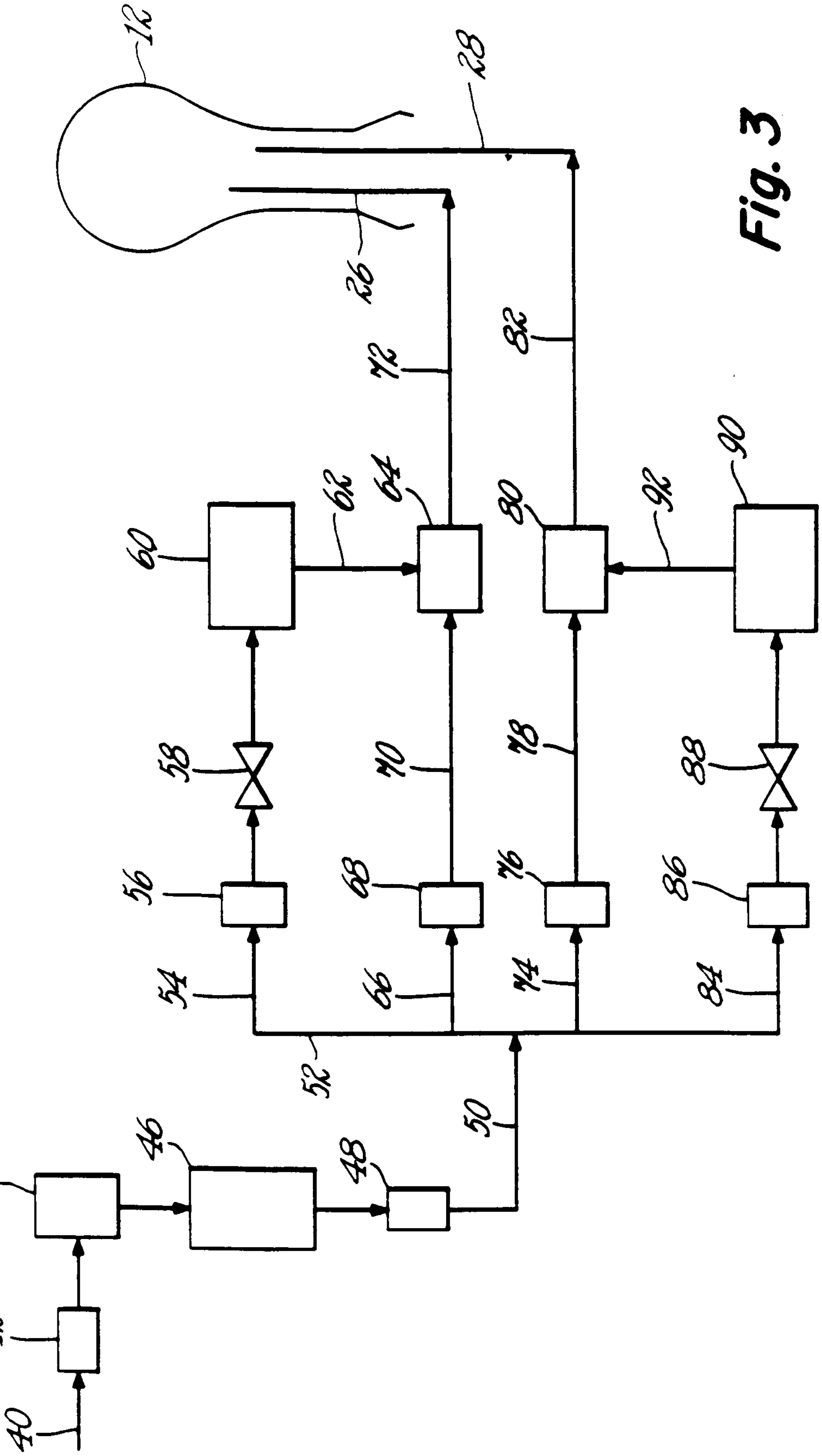
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Fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 1306

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	FR-A-2 304 169 (LABORATOIRE CENTRAL D'ÉCLAIRAGE) * page 2, line 22 - line 28 * * page 3, line 38 - page 5, line 12; figure * ---	1-12	H01K3/00 H01K1/32 H01J61/35
A	US-A-3 352 703 (DOMICONE ET AL.) * the whole document * ---	1-12	
D,A	US-A-4 081 709 (COLLINS ET AL.) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			H01K H01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 May 1994	Schaub, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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