Sept. 22, 1970 W. MEHL ET AL 3,530,325

CONVERSION OF ELECTRICAL ENERGY INTO LIGHT

Filed Aug. 21, 1967 3 Sheets-Sheet 1

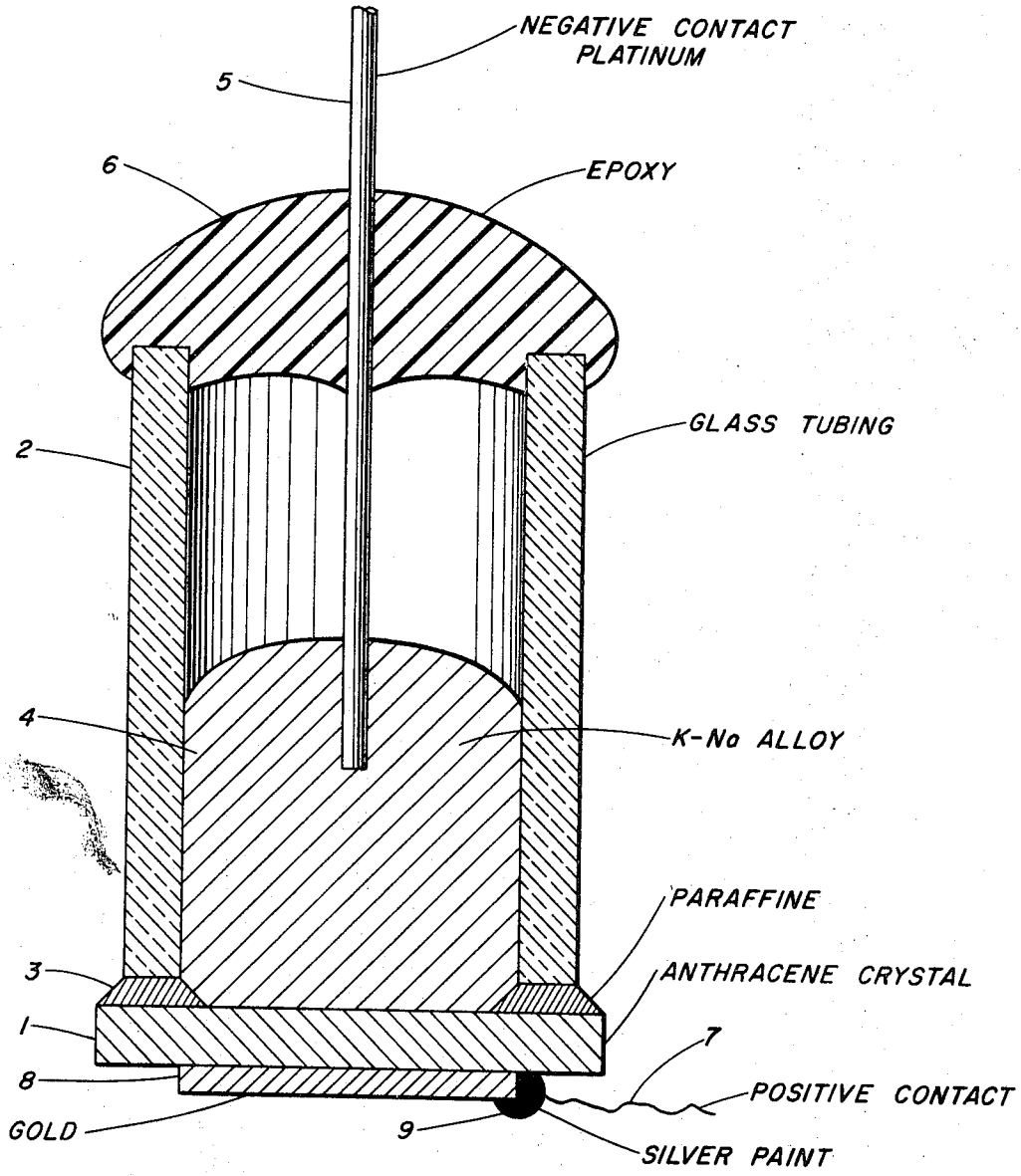



FIG. 1

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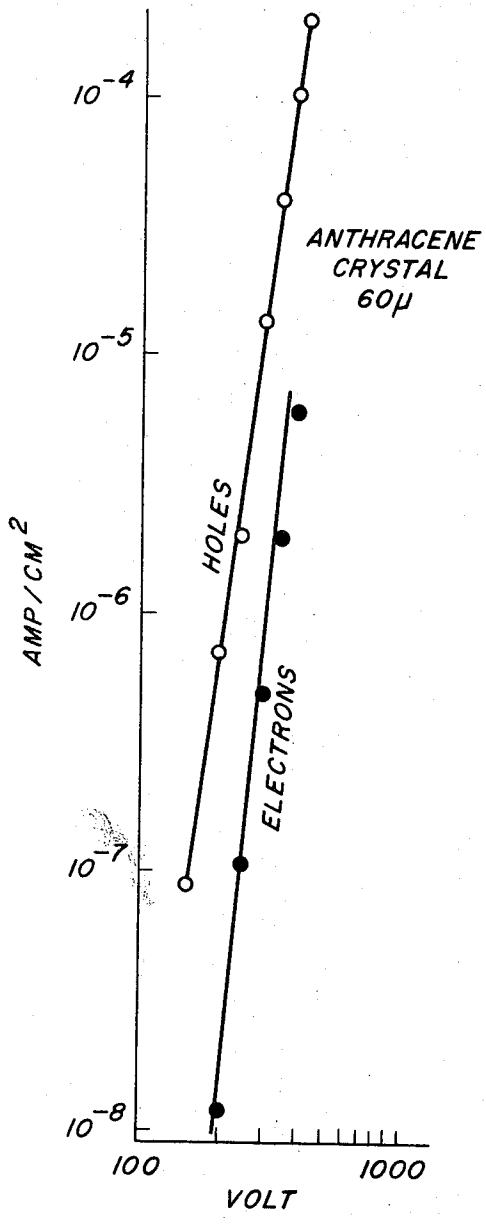



FIG. 2

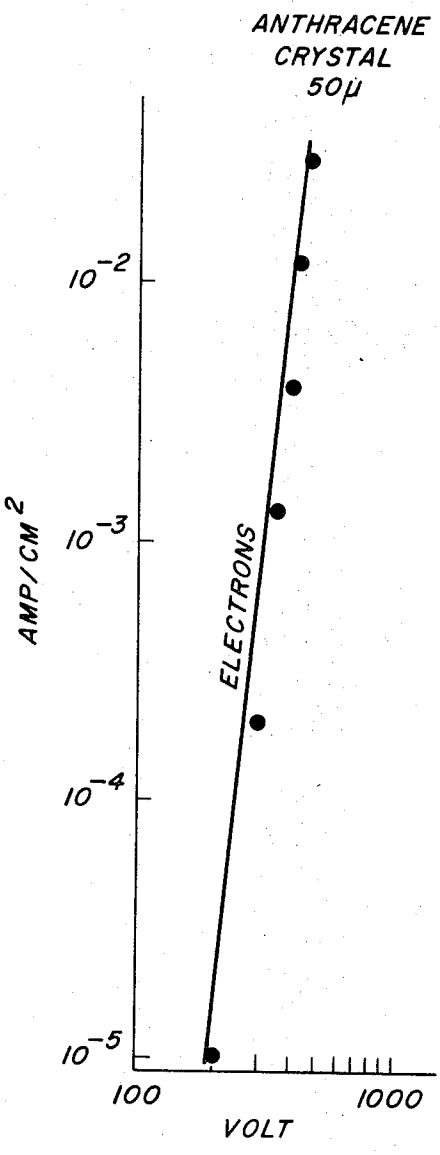



FIG. 3

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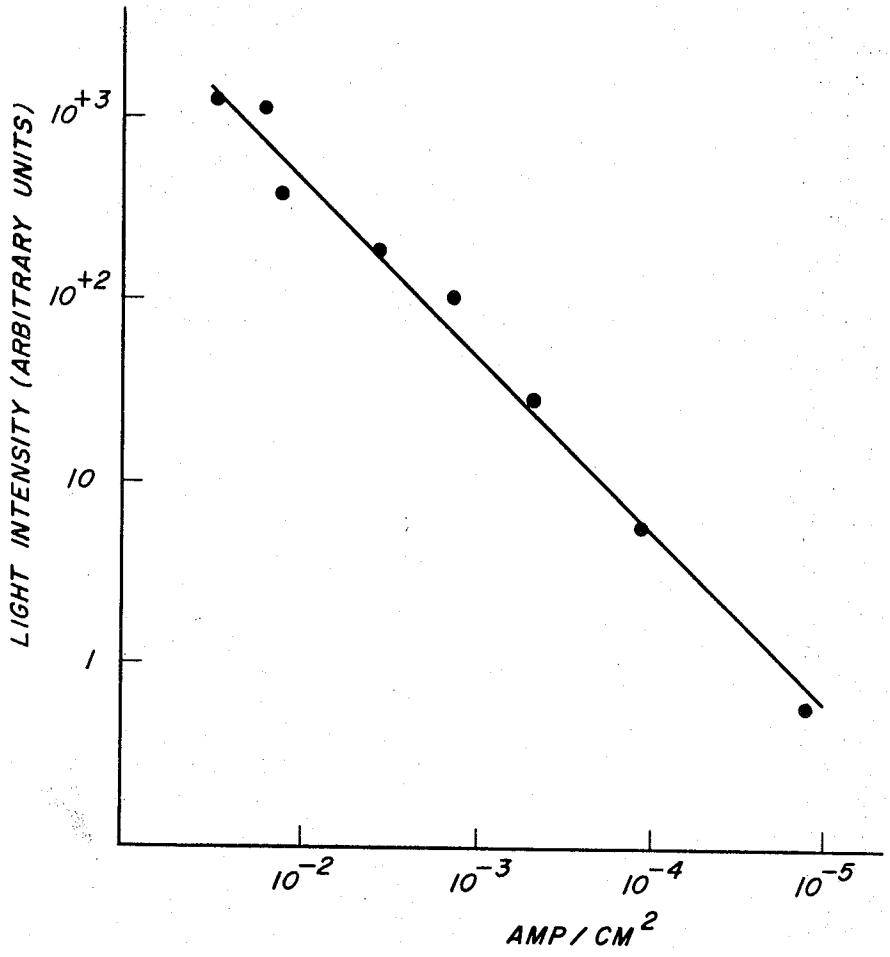



FIG. 4

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3,530,325

# CONVERSION OF ELECTRICAL ENERGY INTO LIGHT

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U.S. Cl. 313—108 12 Claims

## ABSTRACT OF THE DISCLOSURE

A highly purified crystal of a condensed nuclei aromatic hydrocarbon semiconductor, preferably anthracene, is coated on one side with an extremely thin, transparent coating of evaporated gold or a metal having an electronic work function of about 6 electron volts, the other side of the crystal being kept in contact with alkali metal, such as a liquid alloy of sodium and potassium. When a voltage is applied to the two metals, holes are injected from the gold contact and electrons from the alkali metal or other suitable metal or alloy, which has an electronic work function not greater than 2.27 electron volts. The current results in recombination of electrons and holes with uniform radiation of light. The spectrum of the emitted light is identical with the optically excited luminescence spectrum modified at short wavelengths due to internal absorption, i.e. it is blue in the case of anthracene and it shows somewhat different colors in the case of other aromatic hydrocarbons, for example more greenish with perylene.

Light emission is observed uniformly over the contact area and not only at certain isolated spots. The efficiency of light generation is very high, at least 0.2 photon per electron, and a high quantum yield of at least 20% results for a 50$\mu$ thick crystal.

## BACKGROUND OF THE INVENTION

It is also known that holes and electrons can be injected into anthracene through electrolytic contacts and electroluminescence is possible. However, this is primarily of theoretical interest because the electrolytic contacts have to be either strnog reducing or strong oxidizing agents and present the possibilities of reaction with anthracene over a considerable period of time.

## SUMMARY OF THE INVENTION

The present invention utilizes contacts to anthracene or other suitable condensed nuclei aromatic hydrocarbons, such as for example perylene, by utilizing a low work function metal, preferably an alkali metal alloy, such as a liquid alloy of sodium and potassium, on one side of the anthracene crystal and a thin film of gold on the other side. As there is no strong oxidizing agent for the hole injection contact, the hydrocarbon crystal is not destroyed.

The hydrocarbon has to be a semiconductor, i.e. carriers which are injected in the surface can be transported by an electric field through the crystal. This is true of anthracene, perylene, and many other similar condensed-nuclei hydrocarbons. We assume that they are intrinsic semiconductors so that the Fermi level is given by the equation

$$E_F=\frac{E_V+E_C}{2}$$

where $E_C$ is the energy of the lower edge of the conduction band and $E_V$ is the energy of the upper edge of the valence band. Considering a derived quantity having the following representation



$$\Delta=|E_F-E_C|=|E_F-E_V|$$

and representing the electronic work function of the contacting metal alloys as $\phi$, electron injection should then be possible under the following condition

$$|E_F-\phi|\geqq\Delta$$

and hole injection under the condition

$$|\phi-E_F|\geqq\Delta$$

For anthracene the Fermi energy is $E_F=-4.17$ ev. and $\Delta\approx 1.9$ ev., so that electron injection should be possible for metals with

$$\phi\leqq 2.27 \text{ ev.}$$

and hole injection for metals with

$$\phi\geqq 6.07 \text{ ev.}$$

The conditions for electron injection are easily obtained with alkali metals. For practical use, a liquid alloy of about equal parts of sodium and potassium is preferred, but the invention is not limited to this particular metal contact. Obviously, of course, the alkali metal must be protected from reactive substances such as air and moisture, and in the description of the specific embodiments one particular convenient form will be shown. Of course the invention is in no sense limited to this exact design. Electrical contact with the alloy is a simple matter, and a platinum or other wire unattacked by alkali metal can penetrate the liquid alloy. This form of contact is a common one with liquid metal, and the present invention does not differ in the nature of its contact formation from known procedures. It is an advantage that no critical construction is needed.

For the hole injection contact, it has been found, quite surprisingly, that a thin evaporated gold layer operates even though the electronic work function of the gold is only 5.3 electron volts. It is not known why gold, which from the theoretical considerations should not work as a hole injection contact, actually does so; and it is not desired to limit the invention to any theoretical explanation. However, a reasonable possibility is that minor impurities in the surface of the hydrocarbon crystal can result in band bending towards the Fermi level which supports the effect of the work function and causes the gold contact to behave as if it actually had a work function of at least 6.07 electron volts. This explanation is advanced only as a possibility. It has not been proven, and it is possible that other factors are operating. In any event, we are here definitely not dealing with a dielectric breakdown phenomenon because a typical applied field strength is $10^4$ volts/cm., which is at least three orders of magnitude below the breakdown voltage. The fact that the light emission is uniform over the contact area shows that localized breakdown processes at edges, etc. do also not occur.

Since an important use of the hydrocarbon crystal of the present invention is for electroluminescence, for this use the gold contact layer should be very thin, for example of the order of about 200 A., which is substantially transparent in the blue range of the visible light, which is the color of the electroluminescent light produced from anthracene. Thin gold films have slight selective absorption, and so the actual light emerging through the thin gold contact is very slightly shifted toward the green. The shift is so small as to be practically negligible. Contacts can be applied to the very thin gold by conventional means, for example a thin platinum wire applied with a small amount of silver paint. Any other method of attaching electrical contacts to thin gold films may be used, and it is an advantage of the present invention that well known procedures may be employed.

Where the present invention is used for other purposes than for electroluminescence which is to be transmitted through the gold layer it is not necessary that this layer be so thin as to be substantially transparent and for such uses where the transparency is not needed, and in some cases is not desired as where electroluminescence of only an edge of the crystal is to be produced, much thicker gold layers may be employed and are included in the invention. Such layers however are still comparatively thin even though they need not always be sufficiently thin to be transparent.

The efficiency as an electroluminescent device is extremely high; up to 0.2 photon are released per electron, and the quantum efficiency is at least 20%.

While a thin gold film is the preferred hole injecting contact, it may be replaced by a thin film of any other suitable metal which has a sufficiently high work function; for example a thin film of evaporated palladium has been used successfully.

It has been found that the hydrocarbon crystal must be very pure, and in the case of anthracene this can be effected by repeated zone refining procedures, for example 50 times. It is an advantage that the hydrocarbon crystals are not critical in their thickness. However, in order to keep energy losses due to the electric resistance of the materials low, relatively thin crystals are desirable. Thicknesses of from 30 to100$\mu$ give good results. These comparatively thin crystals permit the use of lower voltages which is often advantageous.

## BRIEF DECRIPTION OF THE DRAWINGS

FIG. 1 is a cross-section through a luminescent device according to the present invention;

FIGS. 2 and 3 are curves of current versus applied voltages for holes and electrons in the case of a crystal of 60$\mu$ thickness in FIG. 2 and electrons alone for a 50$\mu$ crystal, and

FIG. 4 is a curve showing light intensity in arbitrary units for different currents.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 shows an anthracene crystal at **1** as cemented onto a tube **2** by paraffin or other suitable insulating cement **3** which is unattacked by alkali metals. A layer **4** of an alloy of 50% potassium and 50% sodium is filled into the bottom of the tube, a negative contact wire **5** of platinum projects into it, the tube is closed off with an epoxy seal **6**. The positive contact is from a wire **7** to a gold film, the connection being by silver paint **9**. The drawing is not to scale, and the thickness of the anthracene crystal, gold positive contact, and paraffin cement are very greatly exaggerated for clearness. Actually, the anthracene crystal is from 30 to 100$\mu$, for example 60$\mu$, and the gold contact of the order of 200 A.

FIGS. 2 and 3 show curves relating current for hole carriers and electron carriers versus voltage for a 60$\mu$ anthracene crystal, and FIG. 3 electron carrier current for a 50$\mu$ crystal. The curves of FIG. 2 and 3 are drawn from accurately measured, individual points, and it will be seen that they are effectively straight lines, the slope of which, however, varies somewhat with the crystal thickness and is also slightly different for electrons and holes, as can be seen in FIG. 2.

FIG. 4 shows the variations of light output with current. The light output is in arbitrary, relative units. An absolute determination of the emitted light intensity was also made and it was found that at least 20% of the electrical energy consumed by the anthracene crystal was emitted as light. Because of the difficulty in measuring the light output with the extreme precision that current can be measured, the experimental points on FIG. 4 do not lie as closely on the curve as in the case of FIGS. 2 and 3. However, it will be seen the curve is actually a straight line within the practical precision of the measurements.



We claim:

**1.** An electroluminescent device comprising in combination,

(a) a thin crystal of extremely pure, condensed nuclei aromatic hydrocarbon having semi-conductor properties,

(b) a negative contact on one side of the crystal, said contact selected from the group consisting of metals and alloys having an electronic work function sufficiently low to inject electrons into the crystals,

(c) means for protecting the negative contact from attack by reactive substances,

(d) a thin film of a metal on the other side of the crystal, the metal constituting a positive contact and having a work function sufficiently high to inject holes into the crystal, and

(e) electrical connections to the negative and positive contacts.

**2.** An electroluminescent device according to claim **1** in which the hydrocarbon is multiple-zone-refined anthracene.

**3.** An electroluminescent device according to claim **1** wherein the negative contact is selected from the group consisting of alkali metals and alloys of alkali metals.

**4.** An electroluminescent device according to claim **3** wherein said negative contact is a liquid alloy of sodium and potassium.

**5.** An electroluminescent device comprising in combination,

(a) a thin crystal of extremely pure, condensed nuclei aromatic hydrocarbon having semiconductor properties,

(b) a negative contact on one side of the crystal, said contact selected from the group consisting of metals and alloys having an electronic work function sufficiently low to inject electrons into the crystal,

(c) means for protecting the negative contact from attack by reactive substances,

(d) a thin film of gold on the other side of the crystal, the gold constituting a positive contact, and

(e) electrical connections to the negative and positive contacts.

**6.** An electroluminescent device according to claim **5** wherein the hydrocarbon is multiple zone-refined anthracene.

**7.** An electroluminescent device according to claim **5** wherein the negative contact is a liquid alloy of sodium and potassium.

**8.** An electroluminescent device according to claim **6** wherein the negative contact is a liquid alloy of sodium and potassium.

**9.** A process for injecting holes into single crystals of substantially pure semi-conducting aromatic compounds having condensed nuclei which comprises contacting the crystal with a layer of a metal selected from the group consisting of gold and palladium and subjecting the crystal to an electrical field.

**10.** A process according to claim **9** in which the aromatic compound is anthracene.

**11.** A process for injecting electrons into single crystals of substantially pure semi-conducting aromatic compounds having condensed nuclei which comprises contacting the crystal with a layer selected from the group consisting of alkali metals and alloys of alkali metals and subjecting the crystal to an electric field.

**12.** A process according to claim **11** in which the aromatic compound is anthracene.

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