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About environmental impact related to the LEDs recycling

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Abstract

In recent years a predisposition of replacing conventional light sources by LEDs appeared, both for interior and exterior lighting systems. Good to know, LEDs are not completely harmless to the environment. As shown below, there are both structural and functional components that, in the absence of some severe recycling procedures, can represent a serious threat for the environment and consequently to the health of living beings.

Rezumat

În ultimii ani s-a constatat tendinţa tot mai accentuată de înlocuire a surselor de lumină clasice cu leduri, atât în sistemele de iluminat interior, cât şi în sistemele de iluminat exterior. Acestea nu sunt însă complet inofensive în privinţa afectării mediului înconjurător. Aşa cum se va vedea în continuare, există atât componente constructive cât şi funcţionale care, în lipsa unor proceduri riguroase de reciclare care trebuie avute în vedere pentru a fi utilizabile la momentul când primele leduri utilizate în sistemele de iluminat îşi vor fi realizat durata de funcţionare, pot constitui un serios pericol pentru mediul înconjurător şi implicit pentru sănătatea fiinţelor vii.

Keywords: LEDs, phosphor, arsenic, aluminium, copper, recycling

1. Introduction

The first inorganic LED sold on the market, in the early 60s, has been based on a gallium arsenic phosphide (GaAsP) chip and was characterized by a 655 nm red radiation at a forward current of 20 mA and its luminous intensity was of 1...10 mcd (therefore it could be used as an indicator LED only).

Afterwards, red colour has been obtained by using gallium phosphide (GaP), resulting in a slight increase in luminous efficacy. [8], [9].

Other colours were obtained during the 70s - green (by using gallium phosphide - GaP, orange and yellow (by using gallium arsenic phosphide - GaAsP).

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A significant increase of luminous efficacy, on one hand and, on the other hand, decreasing forward voltage combined with the use of new materials for LED chip - aluminium indium gallium phosphide (AlInGaP), allowed manufacturers in the 80s to produce various coloured inorganic LEDs – red, orange, yellow and green, characterized by increased luminous flux and improved lifespan. [8], [9].

Blue LED dates from the 90s. This was possible based on a new material for chip construction, namely gallium nitride (GaN). Blue LEDs based on zinc selenide (ZnSe) are characterized by low lifespan and therefore, at least for now, they are not a commercial competitor for blue LEDs whose chips are based on gallium nitride.

The inorganic blue LEDs represented the basis of white LEDs industrial production. [3], [5], [8], [9] Thus, one of the most important ways to obtain white LEDs is that by putting a phosphor layer based on yttrium, the so-called Yttrium Aluminium Garnet (YAG), on the inner surface of the LED die. [8], [9].

According to [8], table 1 summarizes the above presented aspects.

Table 1. Inorganic LEDs structural an functional characteristics (according to [8])

Wavelength λ (nm)	Colour name	Forward voltage (V_F at I_F=20 mA)	LED 5 mm luminous intensity (mcd)	Viewing angle (degrees)	LED die material
660	Ultra-red	1,8	2000 at 50mA	15	GaAlAs/GaAs
635	High efficiency red	2,0	200 at 20mA	15	200 la 20mA
633	Super-red	2,2	3500 at 20mA	15	AlInGaP
620	Super-orange	2,2	4500 at 20 mA	15	AlInGaP
612	Super-orange	2,2	6500 at 20 mA	15	AlInGaP
605	Orange	2,1	160 at 20 mA	15	GaAsP/GaP
595	Super-yellow	2,2	5500 at 20 mA	15	AlInGaP
592	Super pure yellow	2,1	7000 at 20 mA	15	AlInGaP
585	Yellow	2,1	100 at 20 mA	15	GaAsP/GaP
4500 K	„Incandescent" (warm) white	3,6	2000 at 20 mA	20	SiC/GaN
6500 K	Pale (neutral) white	3,6	4000 at 20 mA	20	SiC/GaN
8000 K	Cool white	3,6	6000 at 20 mA	20	SiC/GaN
574	Super lime yellow	2,4	1000 at 20 mA	15	AlInGaP
570	Super lime green	2	1000 at 20 mA	15	AlInGaP
565	High efficiency green	2,1	200 at 20 mA	15	GaP/GaP
560	Super pure green	2,1	350 at 20 mA	15	AlInGaP
555	Pure green	2,1	80 at 20 mA	15	GaP/GaP
525	Acqua green	3,5	10000 at 20 mA	15	SiC/GaN
505	Blue green	3,5	2000 at 20 mA	45	SiC/GaN
470	Super blue	3,6	3000 at 20 mA	15	SiC/GaN
430	Ultra blue	3,8	100 at 20 mA	15	SiC/GaN

2. Method

In order to take into account the effects of chemical elements constituting the inorganic LEDs on human and other living beings, it is necessary to know their physical, chemical and physiological properties.

2.1 Phosphorus (P)

Phosphorus has a high affinity for oxygen and cannot be found free in nature, but only as compounds. These combinations are the following: minerals (apatite), inorganic combinations inside plants and animals ($Ca_3(PO_4)_2$) and animal organic compounds (blood, brain, hair, muscle fibers, egg yolk, milk). [6], [7], [10].

The accumulation of phosphorus inside the human body as tricalcium phosphate - $Ca_3(PO_4)_2$ – is not dangerous, because this chemical substance has no physiological effect on it. But if converted into elemental white phosphorus, the existing amount (about 1 kg) would be enough to kill 10.000 people, considering that the lethal dose for human beings is 100 mg/body. [6].

There are three major allotropic modifications of phosphorus: white phosphorus, red phosphorus and black phosphorus.

White phosphorus is a highly flammable element (ignition temperature is 44^0C, and therefore it is kept under water) and, at the same time, it is very poisonous, due to fact that it is fat – soluble. As physiological effects on the human body, it can cause:

- loss of oxygen in the blood due to its very high affinity for this gaseous chemical element at normal temperature and pressure;
- its ingestion and introduction into the stomach lead to death, but symptoms begin by vomiting and strong stomach pains.

The most commonly used antidote is MgO, but $CuSO_4$ can be used, too. [6].

Chemical properties of white phosphorus in solid and liquid states are dictated by the physical properties of the molecule, which is tetraatomic in regular tetrahedral system, with low valence angles (60^0), resulting in molecule tensioning effect and thus its high reactivity.

Due to its great affinity for metals, the result of the chemical reaction between white phosphorus and metals is the formation of phosphides (phosphorus salts with metals).

As it can be seen in table 1, white phosphorus is the main component in LEDs production based on AlInGaP, GaAsP and GaP.

So far, there are no research studies in chemistry, physics or biology on LEDs derived phosphides behavior in the environment (soil, water, air) and their tendency to dissociation into constitutive chemical elements under different physic - chemical – biological conditions.

2.2 Arsenic (As)

Arsenic represents a very versatile chemical element, allowing the formation of either positive ions (+3, +5) or negative ones (-3), but also other ions with intermediate oxidation states in some cases. [6].

Interestingly, due to the positive electrochemical potential, it doesn't react to hydrogen, however it does as a reducing agent with copper, gold and platinum, firstly generating elemental metals, then forming their arsenides (Cu_2As, Au_2As, $PtAs_2$). [6].

Arsenic is found in nature in two allotropic forms:

- gray or metallic arsenic, a stable form in solid state at any temperature, forming hexagonal crystals, silver, shiny, easily breakable and insoluble in water, carbon disulphide (CS_2) or other solvents. Molecule is tetraatomic, with tetrahedral structure, like white phosphorus molecule; its vapors are highly toxic;
- yellow arsenic is obtained by sudden condensation of the gray arsenic vapors in liquid air; it is unstable, turning to metallic arsenic irreversibly. [6].
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During the LEDs manufacturing process, the chemical reactions between arsenic and other elements from IIIrd main group are really important. Thus, it forms with aluminum, aluminum arsenide (AlAs), and with gallium, gallium arsenide (GaAs).

As it can be seen in table 1, arsenic is the main component in LEDs production based on GaAs, GaAlAs, GaAsP.

Physiological action of arsenic and some of its compounds on human beings is generally harmful.

Thus, large amounts of arsenic represent a strong poison. If left underground, it would turn into arsenic oxide. It has been used since antiquity for cosmetic purpose, but the poison began to be used only in the Middle Ages.

It represents the main component for certain pesticides, human and veterinary drugs, the discolouration of glass and enamels.

Arsenic is classified as toxic and dangerous for the environment in the European Union by Directive EEC 67/548, with subsequent amendments.

Neither in this case there are currently research studies in chemistry, physics or biology on behavior of LEDs derived arsenides in the environment (soil, water, air).

2.3 Aluminium (Al)

Aluminum is the most common metal in the earth's crust (7,4% of its content) [1], [4] but in nature it is not found in the native state, but only in combination as minerals. The most important of them are: silicates and silicoaluminates (clay, feldspar, bleached, mica), cryolite, bauxite, aluminum oxide (alumina), mixed oxides (spinel, chrysoberyl). [6], [7], [10].

The obtaining of aluminium at industrial scale is made by processing bauxite into aluminum, a difficult technological and, at the same time, a high energy consumer process.

Aluminium is a relatively cheap metal compared to the rest of the metals used in industry, being characterized by low density (2700 kg/m^3), excellent thermal and electrical conductivity properties, malleability and ductility.

From the chemical point of view, aluminum is positive trivalent and very reactive with certain metals (except for the reaction with chlorine, it also reacts with oxygen, forming aluminium oxide and with sulphur, forming aluminium sulphide, Al_2S_3).

Being a main component of inorganic LEDs, aluminum is found in the following elements:
- as GaAlAs and AlInGaP, these representing materials for manufacturing LEDs die;
- as a quasi-pure form, if used for heat dissipation radiators, especially required for the operation of the power LEDs.

In terms of physiology, although seemingly harmless, the presence of aluminum in everyday life is responsible for the appearance of the following diseases:
- headache, dyspepsia, aerocolia, asteatosis, anorexia;
- encefalopathy;
- anemia and osteomalacia;
- neurovegetative disorders (Parkinson's, Alzheimer's, Lou Gehrig etc.).
-

European Food Safety Authority (EFSA) warns that exceeding the maximum permissible weekly dose of 1 mg Al/kg can cause very severe disease categories listed above.

2.4 Copper (Cu)

This metal belongs to the category of heavy metals, a group that includes metals characterized by a density of 5000 kg/m^3 (sometimes are considered to be heavy the non-ferrous metals of minimum 4500 kg/m^3 density), which are generally toxic and their residues pollute seriously the environment . [4], [6], [7], [10].

Radiators for power LEDs and circuit boards are made of copper, this metal being better than aluminium in terms of thermal end electrical conductivity. [4], [5].

Copper is found in nature mostly in the form of combinations (sulphides, oxides, carbonates, arsenides) or, very rarely, native, as well as in water, fruits and vegetables. [7].

In terms of chemical valence, copper valence is either +1 or +2 or +3 (rarely). It does not react to water, and being put in contact with atmospheric air, it reacts slowly, forming in the first phase oxide (green). [6], [7], [10].

Regarding the physiological action that copper has on the human body, it can be noted both beneficial and detrimental effects.

The beneficial effects take into account the fact that this metal is essential for life. It is found in all tissues, with role in managing the use of iron in the blood, and it helps with the synthesis of red blood cells. It reduces free radicals action on tissues and it is recommended for prophylactic avoidance occurrence of ailments such as: allergies, alopecia, AIDS, leukemia, osteoporosis, peptic – duodenal ulcer.

The negative effects are due to non-assimilation of copper in the body (copper deficiency). The main problems are: anemia, fragile blood vessels, which can break, damage of internal organs (liver), decreased general immunity, alopecia, gradual whitening skin, chronic fatigue, Wilson disease, Menkes disease, copper toxicosis.

3. Results and discussion

The physiological actions of these four chemical elements and their compounds on the environment and on the living beings are known only partially.

However, research should continue, especially in terms of behavior of phosphides and arsenides underlying the ground, that in some favorable conditions of temperature, humidity, acidity etc. can be decomposed into very dangerous poisons - white phosphorus or arsenic.

Table 2 shows the most possible powerful chemical reactions related to phosphorus and arsenic on the type of the environment. [2].

Table 1. Hazardous products of chemical reactions for phosphorus and arsenic (based on [2])

Chemical element	**Reactant**	**Hazardous products of chemical reaction**
Phosphorus (white)	$KOH + H_2O$	PH_3 (phosphine), very toxic
	Cl_2	PCl_3 (phosphorus trichloride), smokes in the air, suffocating odour, tear effect
	O_2 (insufficient)	P_2O_3 (diphosphorus trioxide), very toxic
Arsenic (metallic)	$AsCl_3$+H_2 or Zn_3As_2+H_2SO_4 (without As)	AsH_3 (monoarsine), very toxic
	AsH_3, warm atmosphere (without As)	As, very toxic
	AsH_3+O_2, full oxidation (without As)	As_4O_6, very toxic
	AsH_3+O_2, incomplete oxidation (without As)	As_4, very toxic
	As_4O_6+C, hot atmosphere (without As)	As, very toxic
	HNO_3+H_2O	H_3AsO_4 (arsenic acid), toxic

It must be checked that aluminum wastes to be recovered and recycled from a screenplay consisting of four stages, as described in fig. 1:

- ***rough selective recovery***;
- ***refined selective recovery***;
- ***packaging and transport to recycling plant***;
- ***obtaining secondary aluminium***.

Energy consumption for obtaining this product (500 kJ/t ... 2000 kJ/t) is lower than the energy consumption for primary aluminum production, this being a very important economic advantage of recycling aluminum.

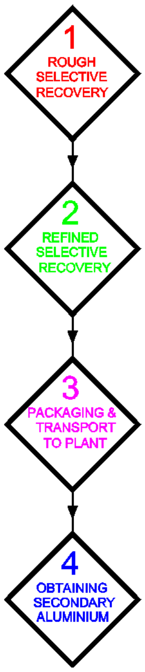

Figure 1. The four stages involved in aluminium recycling.

There was no real concern about global copper reuse and therefore there was no relatively consistent policy of recycling, although a big advantage is that the metal keeps its full purity during technological operations of recycling (melting, see fig. 2). Energy savings obtained from recycling compared to primary copper production directly from the ore, is 85%. However, in 2008 the European countries and Russia have succeeded, without special constraints, to use recycled copper in an amount of 43% of the total used copper.

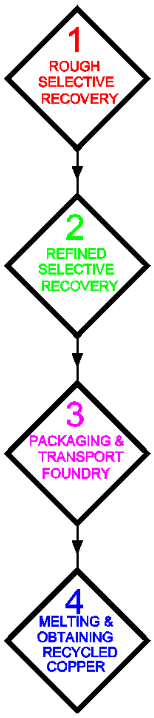

Figure 2. The four stages involved in copper recycling (melting).

4. Conclusions

Within the last two years, there are some concerns worldwide about the recycling of LEDs containing nickel and lead.

However, the present paper aims to warn the public about the other hazardous constituents of the LEDs.

It can be noted that these four constituents of inorganic LEDs and of the related elements (radiators, electronic circuits) can seriously affect the environment and concerning about their recycling must be an imperative of research in the field, even if, for the moment, there is no need for recycling of massive amounts of inorganic LEDs.

Besides the concerns for reducing the environmental impact of toxic waste of phosphorus, arsenic, aluminium and copper, another approach would take into consideration the continuously increasing use of the organic LED (OLEDs) for lighting equipment. The materials used for manufacturing these products are less dangerous for the environment than the materials used for manufacturing inorganic LEDs.

The main types of such OLEDs are:

- small molecular type;
- polymer type.

The efforts of the researchers have to be focused into two main directions:

- to have continuous concerns on the effects of the above mentioned four chemical elements and their compounds on the environment;
- to obtain better technical characteristics of the OLEDs, allowing them to replace the former inorganic LEDs that equip the lighting systems.

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