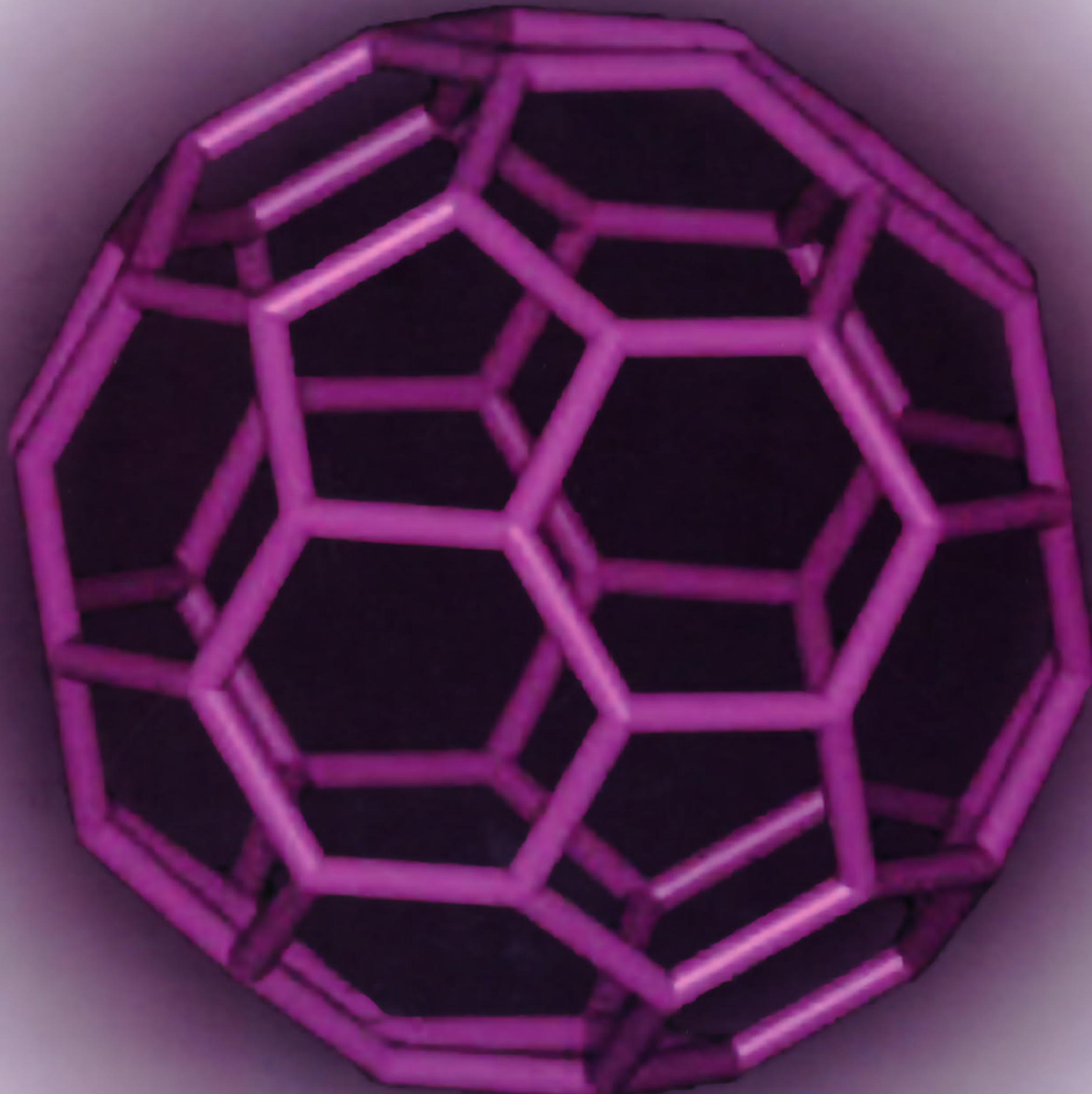

NANOTECHNOLOGY LAW & BUSINESS

Michalitsch & Huebner

The Fullerene Patent Landscape in Europe

Volume 5, Issue 1, Spring 2008

The Fullerene Patent Landscape in Europe

RICHARD MICHALITSCH*, CHRISTIAN KALLINGER*, YVES VERBANDT*, VICTOR VEEFKIND*, AND STEFAN ROLF HUEBNER**[1]

ABSTRACT

Fullerenes, spherical clusters of carbon atoms, are one of the more mature "building blocks" in nanoscience and nanotechnology. Potential commercial applications of fullerenes range from therapeutics to displays to solar cells. Over the last two decades, substantial investments in research and development of fullerenes and fullerene-based products have resulted in large numbers of patents and patent applications. In this article, Richard Michalitsch and his colleagues of the European Patent Office's Nanotechnology Working Group, together with the European patent attorney Stefan Rolf Huebner, provide an overview of the European patenting activities related to fullerenes. They explain the trends in fullerene patenting over time, provide an overview of the fullerene patent landscape, describe specific types of fullerene patents, and identify the key patent holders.

I. INTRODUCTION

In the mid-eighties, Richard E. Smalley, Robert F. Curl Jr. and Sir Harold W. Kroto discovered a new allotrope of carbon, for which they proposed the structure of a hollow sphere of 60 carbon atoms arranged in a lattice of hexagonal and pentagonal rings.[2] Due to the striking resemblance of this structure with the geodesic dome as known from the architecture of Richard Buckminster Fuller, the C_{60} molecule was named after the architect as "*buckminsterfullerenes*" or "*buckyballs.*" In 1996 Smalley, Curl and Kroto were awarded a Nobel Prize for their discovery.

In the early days, the study of buckminsterfullerenes was hindered by the scarcity of the substance. Kroto pointed out that it took him and his colleagues five years to produce a sufficient quantity of buckyballs to prove their theory. Because the buckyballs were in such short supply, it was not viable to

* Richard Michalitsch, Christian Kallinger, Yves Verbandt, Victor Veefkind are members of the European Patent Office's Nanotechnology Working Group (www.epo.org).

** Dr. Stefan Rolf Huebner is a German and European Patent Attorney, representing clients in the field nanotechnology inventions.

1 Corresponding author.

2 H.W. Kroto, et al., *C_{60}: Buckminsterfullerene*, 318 NATURE 162 (1985).

use them commercially. However, in 1990, this all changed when the physicists Wolfgang Krätschmer and Donald Huffman reported in *Nature* that they had succeeded in producing larger amounts of C_{60}. They achieved this by creating an arc between two graphite rods and allowed it to burn in a helium atmosphere. Then they extracted the fullerenes from the carbon condensate formed using an organic solvent.[3]

Now that sufficient quantities of fullerenes were available, an intensive study began into the chemical and physical properties of C_{60} and similar carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}, collectively now known as fullerenes. New substances were produced from these compounds that had new and unexpected properties. An entirely new branch of chemistry was created which inspired other fields of research as diverse as astrochemistry, superconductivity and medicine. Because it appeared feasible now to produce commercial quantities of fullerenes, an interest in the industry was sparked as well for this new class of molecules. It has led to an increasing number of fullerene-related patent applications over the past 15 years. This article will provide an overview of the patenting activities involving fullerenes in Europe.[4]

II. THE FULLERENE PATENT LANDSCAPE

1. Trends in Fullerene Patenting

When fullerenes were first discovered, there was a great deal of excitement about their potential for revolutionary applications, from rocket fuels to carriers that can deliver a drug payload to a precisely defined target inside the body. Much of this initial hype has disappeared as an early breakthrough failed to materialize. Today, fullerenes represent only a small part of the nanotechnology patent landscape - fullerene patents and patent applications account for approximately 2% of all nanotechnology patents and patent applications worldwide. The attention has shifted to the closely related carbon nanotubes,[5] which generate about five times as many applications every year. However, as the increasing number of fullerene patent filings shows, industry continues to devote a fair amount of resources to research in the commercial application of fullerenes.

Figure 1 illustrates the growth in the number of fullerene-related patent families[6] over the past twenty years. Following the *Nature* paper by Krätschmer and Huffman, the annual number of newly filed patent families jumped from very few in 1989 to more than 80 in 1991. Apparently, access to practical amounts of the new material triggered a variety of research activities that were considered to be commercially relevant. The number of filings reached its first peak in 1993, and then in the second half of the 1990s, the number of filings stagnated. A comparable development was observed in the number of scientific publications relating to fullerenes during this period, which also peaked in 1993 and then stagnated.[7]

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3 W. Kraetschmer, et al., *Solid C_{60}: A New Form of Carbon*, 347 Nature 354 (1990).

4 The data presented here has been extracted from the databases of the European Patent Office and the World Patent Index (WPI). The majority of documents that contain keywords related to fullerenes are concerned with other inventions, only touching fullerenes as one possibility amongst many alternative constituent materials for a product. In order to narrow the results down to those patents and patent applications in which fullerenes are indeed essential to the invention, the search for relevant keywords has been confined to the abstracts of the documents. Surprisingly, restricting the search had little impact on the relative distribution of applications with respect to technical fields, time of filing, etc. This suggests that the conclusions presented in this article are relatively robust and independent of the exact definition of a "fullerene invention."

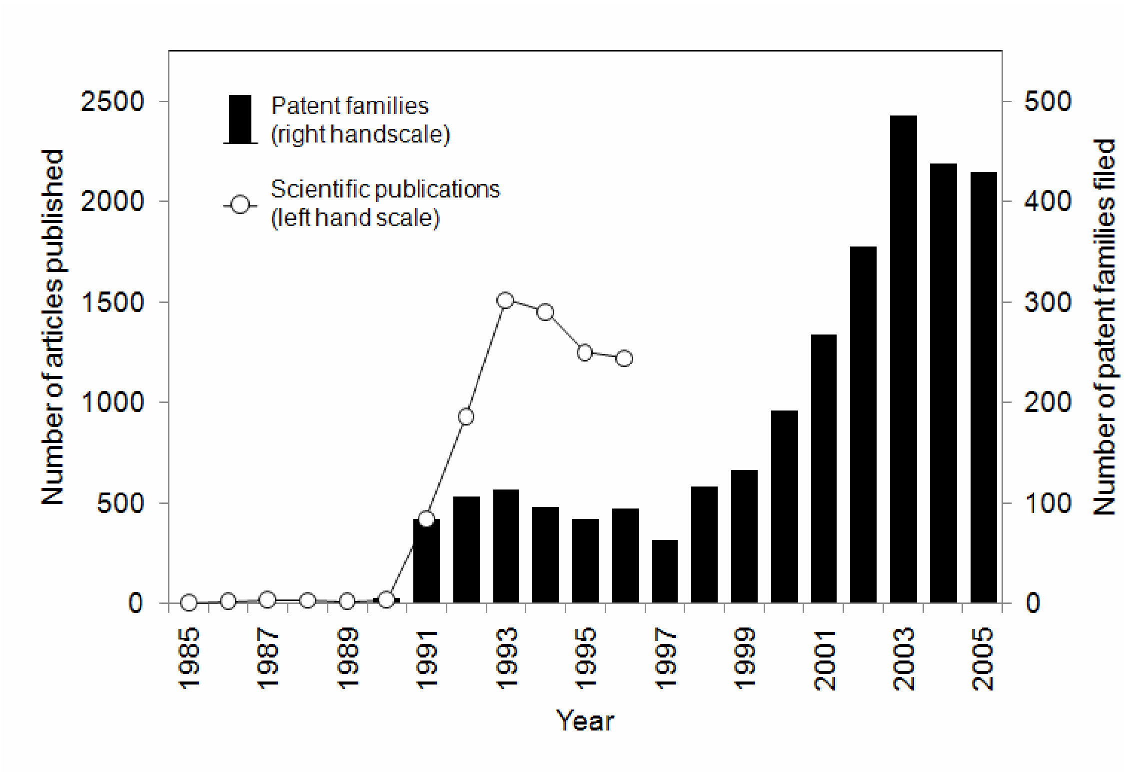
5 J.C. Miller and D.L. Harris, *The Carbon Nanotube Patent Landscape*, 3 NANOTECH. LAW & BUS. 427 (2006).

6 A patent family is a set of patents referring to the same priority application.

7 T. Braun, et al., *Growth and Trends of Fullerene Research As Reflected In Its Journal Literature*, 100 CHEM. REV. 23 (2000) , (providing data for the year from 1985 to 1996).

FIGURE 1: GROWTH OF FULLERENE-RELATED PATENT FAMILIES

The number of fullerene patent families filed by the first filing date worldwide. For comparison, the number of fullerene-related scientific publications between 1995 and 1996 is also shown.



Fullerene patenting gained new momentum in January 2000, when U.S. President Bill Clinton announced his "National Nanotechnology Initiative" with an initial budget of U.S. $230 million, corresponding to an 80% increase in the U.S. government's investment in nanotechnology research and development at that time. Within one year, the number of patent families in nanotechnology in general, and for fullerenes in particular, almost doubled. In 2003, the number of new applications appeared to have entered another period of stagnation—though on a much higher level than in the nineties. Today, about five times as many fullerene inventions are submitted for patent protection in comparison to ten years ago.

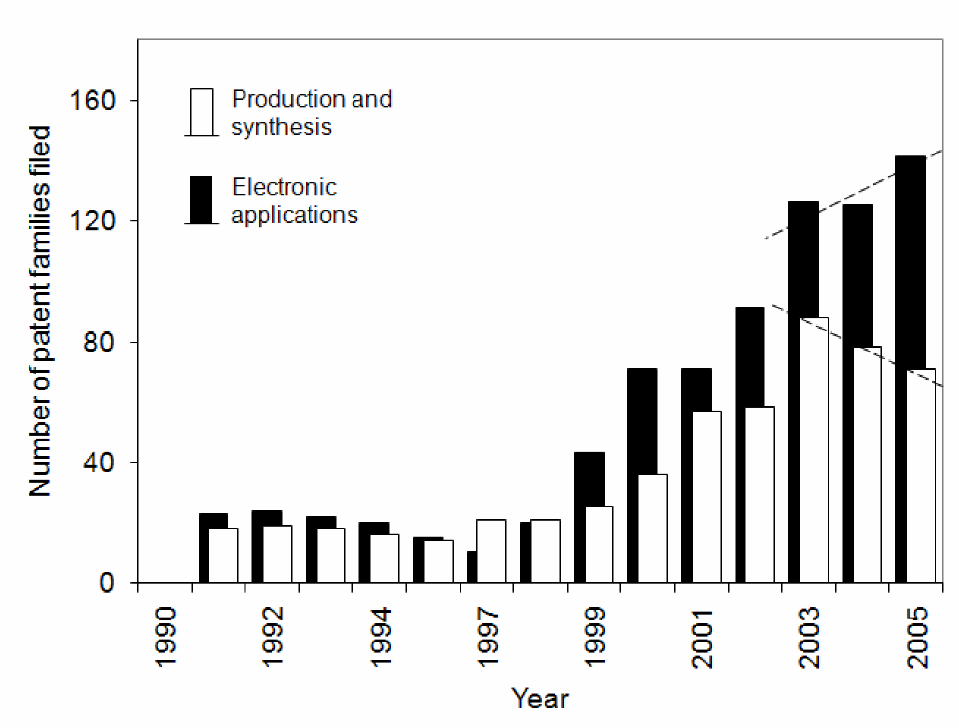
2. Bird's Eye View of the Fullerene Patent Landscape

After Krätschmer and Huffman's initial discovery of the first practical fullerene manufacturing method, roughly half of the early patent applications were concerned with the synthesis of C_{60} and C_{70} fullerenes, derivatives thereof and higher fullerenes such as C_{112}, C_{160}, C_{224} and C_{268}. As the material obtained by these processes was now available for research, a host of newly discovered physical and chemical properties of fullerenes with a potential for commercial exploitation came into focus.

Figure 2 compares the growth in patent filings in the areas of fullerene preparation and synthesis and in the area of electronic applications. Patents concerned with the synthesis and preparation of fullerenes are found in the class C01B of the European Classification System (ECLA), which includes fullerenes *per se* and their manufacturing methods, and the class B01J19, which includes chemical processes involving electric discharges, as commonly used in the larger scale preparation of fullerenes and carbon nanotubes. Electronic applications such as molecular transistors, organic light emitting diodes and solar cells are classified in the patent classes H01L and H01M.

FIGURE 2: COMPARISON OF GROWTH OF FULLERENE PATENT FAMILIES

The worldwide number of patents families filed by the first filing date comparing the synthesis and manufacture of fullerenes[8] (white) with the number of families concerning electronic applications[9] (black).

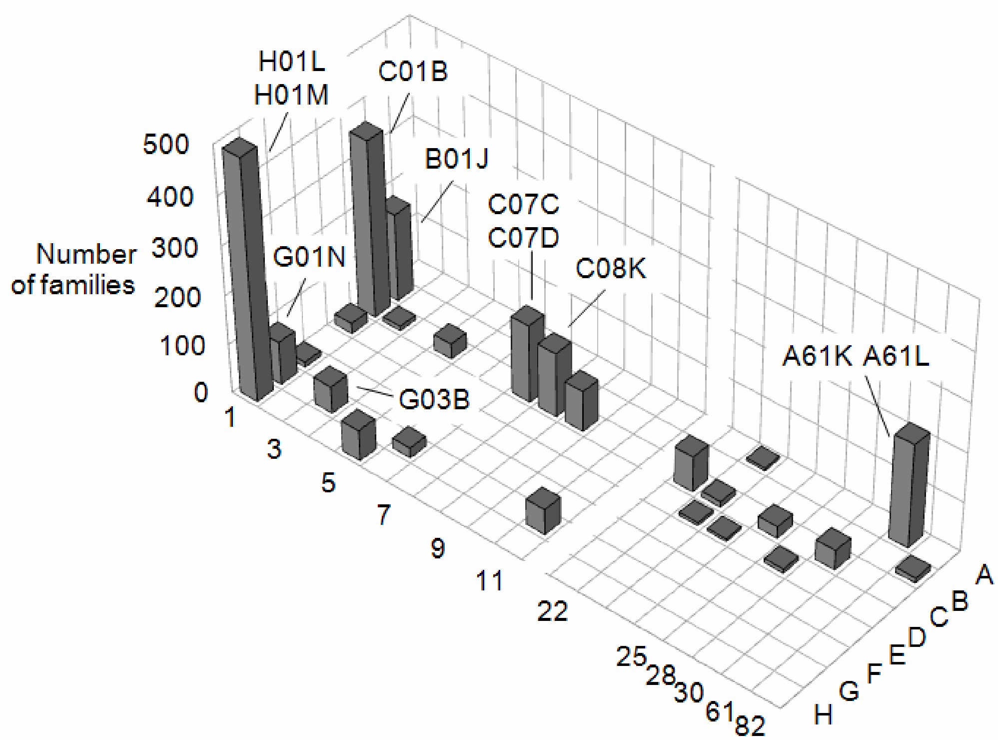


8 Classes C01B31, B01J19, fullerenes *per se* subtracted.
9 Classes H01L and H01M.

The data indicates that up to 2003 both, the number of filings related to fullerene preparation and synthesis and the number of those related to fullerene electronics grew more or less at the same pace. Since 2003, however, a continued rise in electronics filings is contrasted by a decline in the numbers of filings related to fullerene preparation and synthesis. The growing gap illustrates a shift of companies' interest from the simple production of fullerenes towards an increasing number of applications. Preliminary data from 2006 confirms this trend, which might indicate an initial stage of maturity in fullerene science and development.

In Figure 3, the number of patents families is shown as a function of their respective European patent class, thereby revealing the technological areas with the highest activity of fullerene-related patent filing. The prominent columns at B01J, C01B, C07C and D, and C08K mainly show the fullerenes per se, fullerene derivatives and their production methods. Un-modified fullerenes and their production are mostly classified in C01B and B01J; the classes C07C contain some modifications of fullerenes, for example certain derivatives which have been found to exhibit a high anti-microbial and anti-cancer activity; and in C08K patent families directed towards polymers with (modified) fullerenes and polysubstituted fullerenes can be found.

FIGURE 3: DISTRIBUTION OF FULLERENE-RELATED PATENT FAMILIES WITHIN THE EUROPEAN CLASSIFICATION SYSTEM ECLA



The columns H01L and M, G01N, G03D, and A61K and L mostly relate to the inventions directed to applications of fullerenes. The data suggests that the applications shown are essentially confined to a rather limited number of uses directly related to their physical and chemical properties, such as their behavior as semiconductors, heat conductors, antioxidants, radical scavengers or their mechanical strength.

3. Fullerenes, Fullerene Derivatives and Their Methods of Manufacturing

The manufacturing method pioneered by Krätschmer and Huffman relied on an arc discharged between carbon electrodes. This process is still considered to be a powerful method for producing fullerenes on an industrial scale. Sanofi-Aventis holds a substantial number of patents in this area, mostly originating from the former Hoechst AG, which in 1999 merged with Rhône-Poulenc to form Aventis.

More recently the production of fullerenes in high-frequency plasmas has attracted attention in non-patent literature. Interestingly, this did not translate into a corresponding number of patent filings. There are only a few records of patents claiming such alternative production methods. Ideal Star, a company from Japan, manufactures fullerene-inclusion compounds by applying this method. Sony employs similar techniques to modify fullerenes, for example, using nitrogen to produce n-type fullerene polymer films which are then used as an electronic-receiving layer in photodiodes. European companies and institutions do not appear to be active in the field.

The presence of fullerenes in flames was discovered as early as 1987,[10] only two years after Smalley, Curl and Kroto's had described buckyballs for the first time. However, our analysis has revealed that there are only about 20 records of patent applications in the 1990s where combustion based methods for producing fullerenes were used. In 2000, this number suddenly jumped to roughly 50 applications per year. This significant increase was accompanied by a notable loss of interest in arc-discharge based methods as the number of new applications in this area fell to practically zero. Mitsubishi Chemical is the leading worldwide applicant of patents concerning combustion-based fullerene manufacture. In Europe, Cinvention AG and the independent inventor, Till Keesmann (Argus Holding) have small patent portfolios in this area.

4. Applications of Fullerenes

The classes H01L and H01M, which cover solid state electronic devices using organic materials as the active part or hybrid devices of organic and inorganic structures, represent the most active area in fullerene patenting at present. These classes include devices ranging from single electron transistors to photovoltaic cells. In the latter case, the photovoltaic module is typically based on a heterojunction composite material that comprises of C_{60} or other types of fullerenes.

Due to their electrical properties, the fullerenes can also be used as sensing elements in electrochemical sensors, which are classified in the class G01N. This class also covers patents concerning conventional analytic assays or immunoassays which do not rely on fullerenes as sensing elements but where the fullerenes have another purpose, e.g. that of adsorbents, support for enzymes as biocatalysts, chromatographic matrices or other separation media for the separation of biomolecules, backbones in biomimetic systems for molecular recognition, and support for the covalent immobilisation of proteins, in particular antibodies, or DNA.

With regards to the fullerene's unique optical properties, the majority of the patent applications seek to exploit their ability to strongly absorb visible and ultraviolet light. There are a number of patent applications used for highly light absorptive nano-composites, where fullerenes and polymers are mixed

[10] P. Gerhardt, et al., *Polyhedral Carbon Ions In Hydrocarbon Flames*, 137 CHEM. PHYS. LETT. 306 (1987).

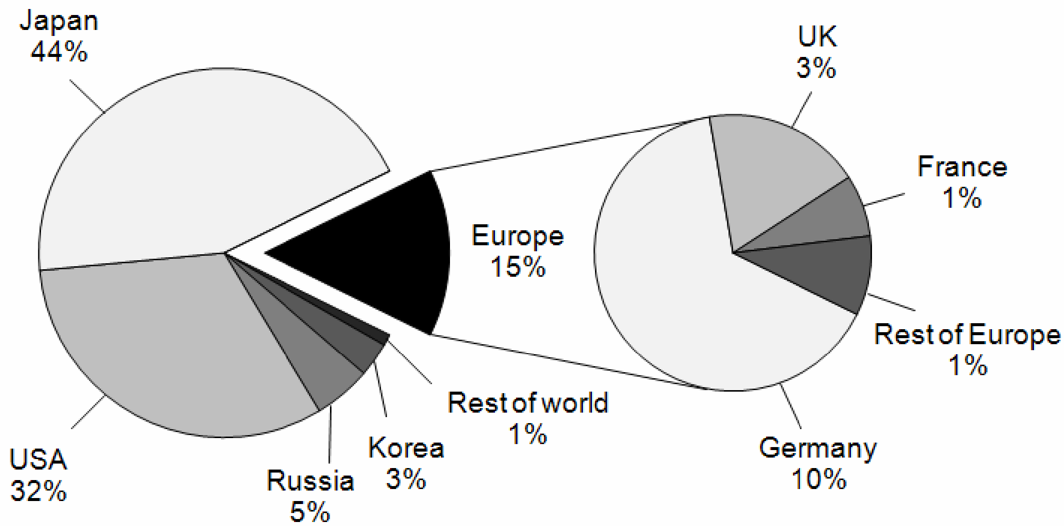
to provide light absorbers, for example, display applications, which can be found in the class G03B, and sunscreens, which are classified in the patent class A61K.

The class A61K, which corresponds to preparations for medical, dental, or hygienic related purposes, is in fact another prominent area of fullerene-related patenting. In particular, cosmetic compositions containing fullerenes have been filed for patenting in a variety of applications ranging from skin care products to hair conditioners. Most inventors seek to exploit both the fullerene's radical scavenging and anti-oxidative behaviour and their light absorbing and reflecting properties. In this field, the French cosmetics giant L'Oreal is one of the worldwide leading applicants. General Electric, Mallinckrodt Medical Inc., Microspherix and others hold patents or patent applications regarding the use of modified fullerenes in combination with contrast agents in magnetic resonance imaging. Tego Biosciences (formerly known as C Sixty) holds a variety of patents and patent applications related to the use of derivatized fullerenes as anti-apototic drugs to treat central nervous system disorders and other diseases.

5. European Patent Applicants

The research and development in Europe of fullerenes is rather small compared to the activities in Japan and the United States. This is reflected by the relatively small share of fullerene-related European patent applications in our sample that have been filed by European applicants. As shown in Figure 4, more than three quarters of all applications filed with the European Patent Office originate from Japan or the United States. European applicants only contribute to a meager 15%. Breaking the European contribution down by country reveals that the majority of these inventions come from Germany.

FIGURE 4: BREAKDOWN OF THE ORIGIN OF FULLERENE-RELATED PATENTS WORLDWIDE



Between 300 and 400 businesses, research institutions, universities and independent inventors in Europe hold patents or patent applications relating to fullerenes, but only 30 of them hold more than one or two. Established companies as well as start-ups and public academic and research institutions rank amongst the leading applicants. Sanofi-Aventis heads up the list by virtue of its large portfolio of patents directed towards methods of fullerene production. Konarka,[12] the number two in the list, focuses on the use of fullerenes in photovoltaic cells. The list includes several publicly funded institutions in Germany and France, clear evidence of the fact that fullerene research and development still heavily relies on public sources of financing.

TABLE 1: TOP 20 EUROPEAN APPLICANTS OF FULLERENE-RELATED PATENTS AND THEIR TECHNICAL FOCUS

	Applicant	*Country*	*Type*	*Technical Focus*
1	**Sanofi-Aventis**[13]	France/ Germany	Business	Industrial scale manufacturing of fullerenes
2	**Konarka Technologies and Konarka Austria Research and Development**[12]	USA	Business	Flexible photovoltaic cells
3	**Hahn-Meitner Institut**	Germany	Public research institution	Molecular electronics, memories, field-effect transistors (FETs), production of endohedral fullerenes
4	**Asea Brown Boveri (ABB)**	Switzerland	Business	Filling materials for separation columns, cables with high mechanical strength and temperature resistance, nanostructure conductors with high electrical conductivity, protective coatings for high voltage installations, degradation-protection of organic materials
5	**Centre National de la Recherche Scientifique (CNRS)**	France	Public research institution	Nano-composites, diamond-like materials
6	**Technische Universität of Dresden**	Germany	Academic institution	Organic semiconductor materials, organic solar cells, temperature sensitive Nuclear magnetic resonance (NMR) materials
7	**Cinvention**[14]	Germany	Business	Biocompatible materials and surfaces for implant coatings and drug delivery, porous materials (e.g. for gas separation)

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12 Konarka has been included in this list despite it being a U.S. company, because most of its fullerene-related applications were filed in the name of its Austrian research centres or in the name of Quantum Solar Energy Linz (QSEL), which has been acquired by Konarka in 2004.

13 Formerly Hoechst AG.

14 Formerly Blue Membranes GmbH.

	Applicant	*Country*	*Type*	*Technical Focus*
8	**Bosch**	Germany	Business	Thermally stable lubricants, sealing for gas sensors
9	**Commissariat d'Energie Atomique**	France	Public research institution	Thermally stable sinter materials, photoactive materials (for solar cells), functionalized surfaces
10	**Artur Fischer Werke**	Germany	Business	Polymer composites for fixing elements, raw plugs
11	**Koninkl Philips Electronics**	Netherlands	Business	Solar cells, organic light-emitting diodes (OLEDs), displays, diamond like materials
12	**L'Oreal**	France	Business	Hair cosmetics, make-up, sunscreens
13	**Bayer**	Germany	Business	Hydrogenation catalysts, catalytically active electrodes for fuel cells
14	**BASF**	Germany	Business	Polymer composites, low-wear thermoplastic materials, rigid polyurethane foams
15	**Patterning Technologies**	UK	Business	Ink compositions for printing patterned electronic devices
16	**Alcatel**	France	Business	Polymer composites for the coating of optical fibres
17	**Degussa**	Germany	Business	Compositions for solvent-borne inks, water-borne inks, inkjet inks, xerographic toners and coatings
18	**Armines**	France	Public research institution	Fullerene synthesis
19	**Till Keesmann (Argus Holding)**	Germany	Business	Synthesis of endohedral fullerenes
20	**Fraunhofer Gesellschaft**	Germany	Public research institution	Flexible integrated polymer chips, electrically conducting polymer composites

III. CONCLUSION

Fullerene research has so far failed to develop the commercial potential originally hoped for. Fullerenes today represent only a small part of the vast nanotechnology patent landscape. However, fullerene-related patenting activity has increased over the years. Recently, the number of filings concerning applications of fullerenes is growing while filings for inventions related to the fullerene preparation and manufacture are declining. This could possibly indicate an initial stage of maturity in the fullerene field.

With regards the production methods, the current focus is on combustion-based processes. The majority of activity in the applications of fullerenes is currently in the area of solid-state electronic devices, electrochemical sensors, medical preparations and cosmetics. European applicants have a relatively small share of patent filings in the fullerene domain in comparison with American and Japanese applicants. Fullerene research heavily relies on public funding and consequently there are a number of public institutions amongst the leading European applicants.