A Chemistry Field in Search of Applications Statistical Analysis of U.S. Fullerene Patents

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Received February 27, 2002

The paper is examining the U.S. patenting activity on the application of fullerenes and shows that despite some pessimistic manifestations in this respect in the current literature there are many promising approaches regarding the pragmatic aspects of this field of chemistry.

INTRODUCTION

In recent papers[1,2] we have examined the growth and trends of the journal literature of fullerenes research, from the discovery of fullerenes in 1985 up to 1998. The results showed that fullerenes have evolved into a dynamical interdisciplinary field, adding important new contributions to our general knowledge of natural sciences.

Even though these previous studies have focused on research rather than applications, we disagree intuitively with the following views of Calvert[3] related to fullerene applications: "*fullerenes are an example of promises unfulfilled. Given a totally new material, researches envisage many possible uses (molecular ball bearings, for lubricants) where the fullerenes might be the best option. But from superconductors to lubricants, fullerenes have not yet improved on existing materials*".

To obtain evidence that supports our intuitive conclusions, we have decided to examine a critical literature that focuses on potential fullerene applications, that of patents. Specifically, this paper will use statistical indicators on patents, supported with specific examples, to refute Calvert's (and others) skepticism.

APPROACH

We have used the U.S. Patent and Trademark Office Database as the primary reference source. Selection of fullerene patents was based on using appropriate keywords developed during a previous fullerenes research study.[2] The citation data were extracted from the CD-ROM Edition of the Science Citation Index (of the Institute for Scientific Information, Philadelphia, PA) as used in ref 1.

RESULTS AND DISCUSSION

In this paper, we considered the distribution of the calculated patent indicators by the country of origin of the inventors and the assignee of the patents, by the company of the assignee, by cooperation between countries in the inventions in question, by productivity of the inventors, and by the subfield classification of the inventions. To illuminate the interaction between basic research as reflected in publishing, and applications as reflected in patenting, the most cited journal papers and journals in the patents are also presented.

Table 1

rank	inventor's country	no.of patents
1	U.S.A.	453
2	Japan	82
3	Germany	29
4	Canada	16
5	France	14
6	Australia	11
7	Israel	10
8	Switzerland	10
9	Great Britain	9
10	Taiwan	8
11	Norway	6
12	Netherlands	4
13	Croatia	2
14	Finland	2
15	Korea	2
	10 countries	1

A total of 618 patents were retrieved from the database, and all were judged relevant to the fullerene field.

A. Countries of Inventors and Assignees. Inventors from 25 countries contributed to the patenting of fullerenes (Table 1). The assignees of these patents are from 17 countries (Table 2). Comparing the two country lists with each other and with our earlier results on the journal activity of countries in the fullerene research field,[1,2] we can find a consistent top three position for the U.S., Japan, and Germany. France is among the top seven in all four lists. Remarkably, Russia, China, and the U.K., while among the top producers in journal papers publication, are missing from the U.S. patenting lists— presumably because they have their own, different patenting channels. On the other hand, the patenting activity of Australia and Canada is much beyond their share from publications. There is a strikingly high number of individual inventors from Israel; the distinguished position

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10.1021/ci0200117 CCC: $22.00
Published on Web 08/14/2002

Table 2

rank	assignee's country	no. of patents
1	U.S.A.	406
2	Japan	92
3	Germany	33
4	France	10
5	Canada	9
6	Australia	8
7	Luxembourg	5
8	Taiwan	5
9	Israel	4
10	Norway	4
11	Great Britain	3
12	Switzerland	3
13	Croatia	2
14	Austria	1
15	Hong Kong	1
16	Slovakia	1
17	Sweden	1

Table 3

rank	assignee	city	no. of patents
1	University of Texas System	Austin, TX (U.S.A.)	22
2	University of California	Oakland, CA (U.S.A.)	21
3	Pharmacyclics, Inc.	Sunnyvale, CA (U.S.A.)	19
4	Xerox Corporation	Stamford, CT (U.S.A.)	18
5	IBM Corp.	Armonk, NY (U.S.A.)	17
6	Du Pont de Nemours & Co.	Wilmington, DE (U.S.A.)	15
7	Exxon R&E Co.	Florham Park, NJ (U.S.A.)	13
8	Hoechst AG	Frankfurt (Germany)	13
9	NEC Corp.	Tokyo (Japan)	13
10	SRI International	Menlo Park, CA (U.S.A.)	13
11	Silverbrook Research Pty Ltd	Balmain (Australia)	10
12	Agency of Industrial S&T	(Japan)	8

of Luxembourg in the list of assignees is due to one single company

Two different models ("paradigms") can be emphasized:

(1) U. Texas, Austin: One single inventor (J. L. Sessler) is involved in most of the patents; the California-based Pharmacyclics, Inc. is always present as coassignee. It is a typical university−industry cooperation mediated by a small group of individuals. In total, however, 21 persons are involved as coinventors, nine of them are from the University ["centralized model"].

(2) U. California: Fifty-three inventors contributed to the 21 patents. Thirty-eight of them California-based: none of them contributed to more than four patents, 30 occurred only once. No relation to industrial firms can be revealed ["scattered model"]. It would require deeper case studies to reveal the rationale behind these models and their validity. The samples here are rather small to draw any far reaching conclusions.

B. Patenting Companies and Institutions. As shown in Table 3, it is somewhat surprising that universities are leading the list of fullerene patenting. As expected, the U.S. leads the list of the patenting companies, although Germany, Japan, and Australia, are quite active in patenting. Although high on the basic research articles productivity list, one can meditate why the patenting activities of companies and institutions from the U.K., France, Switzerland, and Italy are so modest.

C. International Coinventing Patterns. Although international cooperation is a well-known trend in basic research papers in science, and is clearly visible also in fullerene research, Table 4 shows that country co-INVENTING (INVENTORS FROM MORE THAN A SINGLE COUNTRY) is quite restricted as compared with single country activities. It is, however, remarkable that relatively small countries (Israel, Switzerland, The Netherlands, Norway, Finland) appear to be quite diligent in this respect. What seems remarkably low is the co-INVENTING activities of countries in which the U.S. is not involved. It is difficult to draw any reliable conclusions, but the lack of England, Japan, and Australia is striking, anyway.

Table 4

cooperating countries	no. of patents
U.S.A. + Canada	8
U.S.A. + Israel	7
U.S.A. + Switzerland	5
U.S.A. + France	4
U.S.A. + Netherland	4
U.S.A. + Germany	3
U.S.A. + Norway	3
U.S.A. + Finland	2
U.S.A. + 10 countries	1
Austria + Germany + Slovakia	1
Canada + France	1
France + Switzerland	1
Great Britain + Japan	1

D. Individual Inventors' Productivity. Table 5 presents the most prolific inventors. It is interesting to compare these data with our earlier results in authors' journal papers publication productivity. Among the most productive 108 authors in fullerene science (ref 1, Table 3), only one (Y. Wang) is present in the top inventors' list. Twenty-five others had at least one U.S. patent inventorship. From the top seven most prolific authors of ref 2, only one (R. E. Smalley) can be found in the U.S. patent inventors' list. From another perspective, 10 of the 15 most prolific inventors of Table 5 have no publications listed in our peer-reviewed fullerene science and technology publication databases. It seems that there is a common pool of potential authors and inventors, but particular skills and strict specializaton are required for reaching eminence in either direction.

In 1926 Lotka[4] proposed an inverse-square law relating authors of scientific papers to the number of papers written by each author. Lotka was interested in determining "*if possible, the part which men of different calibre contribute to the progress of science*". Lotka plotted the number of authors against the number of contributions made by each author on a logarithmic scale and found that in each case the points were closely scattered about a straight line having a slope of approximately two. On the basis of these data, Lotka deduced the general equation

$$mn^c = k$$

where m is the fraction of authors making n contributions each, and c and k are constants.

Lotka[4] summarized his findings: "*In the cases examined, it is found that the number of persons making 2 contributions is about one-fourth of those making one; the number making 3 contributions is about one-ninth, etc; the number making n contributions is about 1/n² of those making one; and the proportion of all contributors, that make a single contribution, is about 60%*".

Table 5

rank	inventor	assignee	no. of patents
1	Sessler JL	University of Tex. Sys. (Austin, TX)	20
2	Magda D	Pharmacyclics, Inc. (Sunnyvale, CA)	14
3	Hemmi GW	Pharmacyclics, Inc. (Sunnyvale, CA)	11
4	Mody TD	Pharmacyclics, Inc. (Sunnyvale, CA)	11
5	Chiang LY	Exxon Research and Engineering Company (Florham Park, NJ)	10
6	Silverbrook K	Silverbrook Research Pty. Ltd (Sydney, AU)	10
7	Ullman EF	Snytex (U.S.A.) Inc. (Palo Alto, CA)	10
8	Gruen DM	1324 59th St. (Downers Grove, IL)	8
9	Wang Y	E. I. Du Pont de Nemours and Company (Wilmington, DE)	8
10	Ziolo RF	Xerox Corporation (Stamford, CT)	8
11	Sekhar JA	University of Cincinnati (Cincinnati, OH)	7
12	Betz WR	Supelco, Inc. (Bellefonte, PA)	6
13	Desorcie JL	Supelco, Inc. (Bellefonte, PA)	6
14	Dyer MJ	SRI International (Menlo Park, CA)	6
15	Tanaka S	Shun-ichiro (Kanagawa-ken, JP)	6
	22 inventors		5
	47 inventors		4
	71 inventors		3
	223 inventors		2
	719 inventors		1

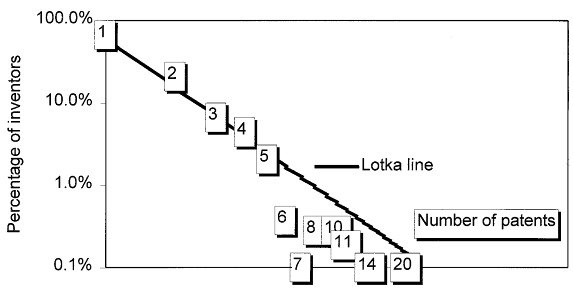

Figure 1. Lotka distributions in U.S. fullerene patents.

In other words, for every 100 authors contributing 1 article each, there would be 25 others contributing 2 articles each (100/22 = 25), about 11 contributing 3 articles each (100/32 = 11.1), about 6 contributing 4 articles each (100/42 = 6.25), and so on.

Lotka's law can also be expressed by the equation

$$a_n = a_1/n^2, \quad n = 1,2,3....$$

where a is the number of authors contributing n papers each. De Solla Price[5] has suggested that one-half of all the scientific papers is contributed by the square root of the total number of scientific authors.

We were interested to know whether Lotka's law can be applied to inventors' productivity as well. Figure 1 shows that this is indeed the case. At the individual level, productivity of journal papers or patents follows similar social laws.

E. Citation Analysis in Patents. Science, whether viewed as a social or an intellectual system, is essentially self-organizing. The very process of doing science—creating and communicating new knowledge—generates structure, whether in terms of the interrelations of ideas or of informal communication among scientists. The difficulty is that this structure is an "invisible" one. It is the result of many small and somewhat private thoughts or actions, the collective outlines of which remain obscure. One "visible" manifestation of these thoughts and actions is citations appearing as references in scientific papers and books. Whether citations in patents have a similar role is an open question. Tables 6 and 7 provide evidence of the linkage between basic and applied research and the interaction between the two. Each of the 12 top cited papers of Table 6 are fairly highly cited in the journal literature, as well. Papers ranked 1, 4, 6, 7, and 10 in Table 6 are ranked 1, 2, 4, 6, and 16, respectively, among the fullerene papers most cited in 1985−1998 in the journal literature.[1] The other papers are missing from this latter list partly because they are not primarily fullerene papers, partly because of their educational rather than scientific nature.

Table 6

rank	cited paper	times cited
1	Kratschmer: *Nature* 347 (1990) 354	59
2	Marks: *J. Am. Chem. Soc.* 100 (1978) 1695	39
3	Shelton: *Inorg. Chem.* 30 (1991) 4295	36
4	Kroto: *Nature* 318 (1985) 162	30
5	Curl: *Sci. Am.* (1991) 54	29
6	Iijima: *Nature* 354 (1991) 56	27
7	Haufler: *J. Phys. Chem.* 94 (1990) 8634	25
8	Sessler: *Acc. Chem. Res.* 27 (1994) 43	21
9	Sessler: *Inorg. Chem.* 28 (1989) 1333	21
10	Ebbesen: *Nature* 358 (1992) 220	21
11	Mastruzzo: *Photochem. Photobiol.* 60 (1994) 316	21
12	Sessler: *Tetrahedron* 48 (1992) 9661	21
	3399 other papers	8611
	unidentifiable sources	1478

Table 7

rank	journal	times cited
1	*J. Am. Chem. Soc.*	1059
2	*Nature*	493
3	*Science*	439
4	*J. Chem. Soc., Chem. Commun.*	326
5	*Angew. Chem., Int. Ed. Engl.*	246
6	*J. Org. Chem.*	238
7	*Inorg. Chem.*	227
8	*J. Phys. Chem.*	227
9	*Appl. Phys. Lett.*	218
10	*Proc. Natl. Acad. Sci. U.S.A.*	182
11	*Biochemistry*	176
12	*Tetrahedron Lett.*	161
13	*Anal. Chem.*	118
14	*Chem. Phys. Lett.*	116
15	*Gene Regul. Biol. Antis. RNA DNA*	100
	683 other titles	4652
	unidentifiable sources	1461

Table 8

international patent classification category	no. of patents
electricity	131
instruments	106
inorganic chemistry	80
organic chemistry	78
metallurgy	46
organic macromolecular compounds	46
processes/apparatus	38
health	34
separation/mixing	30
printing	25
biochemistry	21
petroleum, gas	17
textiles	17
dyes, paints, polishes	10

F. The Technological Fields to Which the Fullerene Patents Are Dedicated. As shown in Table 8, the potential technological applications of fullerenes are truly of an interdisciplinary nature. It is perhaps not surprising that given the special electrical properties of these molecules the applications in the field of electricity are topping the list. The relatively modest number of health applications is somewhat disappointing and could be due in part to the water insolubility of pristine fullerenes. However many functionalized fullerenes and supramolecular fullerene host–guest compounds which are water soluble were synthesized recently, and it is very probable that they will find their way into direct medical applications. In addition medicine has become very high tech, and fullerene applications to electricity, biochemistry, etc., may very well also find their way into medical applications. In the patenting activities of companies, their topical interests are very visibly reflected (see Chart 1).

SUMMARY AND CONCLUSIONS

Based on analysis of the U.S. patent database, the following conclusions can be drawn about the discipline of fullerenes. The U.S., Japan, and Germany are the patenting leaders, as they were in journal publications analyzed previously, and France is a prolific patenter as well. Russia, China, and the U.K., prolific in the published literature, are significantly under-represented in the patent literature. Other patent databases need to be examined to ascertain whether these countries do not patent at all or choose not to patent in the U.S.

In contrast with the previous perspective of universities having minimal applications focus, universities are leaders in fullerene patenting institutions. Country copatenting is quite restricted as compared with single country patenting activities. There is some overlap between authors and inventors, especially at the lower productivity levels, but the most prolific authors and inventors appear to be drawn from almost two disjoint categories.

Patent productivity appears to follow an inverse square law, similar to that of published papers. Papers that are highly cited in the journal literature are highly cited in the patent literature as well. Since these highly cited papers tend to reflect rather fundamental fullerenes research, the data provide evidence of a confirmed link between technology applications and fundamental science.

Chart 1. Topical Patenting of U.S. Companies

Fullerene-polymer compositions
Composites with interphases
Fullerene-grafted polymers
Polysubstituted fullerenes and their preparation
Method of making metal fulleride
Fullerene compositions and preparation
Substituted fullerenes as flow improvers
Free radical adducts of fullerenes with hydrocarbons and polymers
Synthesis of microporous ceramics

IBM (main direction: electronic applications)

Atomic scale electronic switch
Process for making fullerenes
Apparatus for photorefractive two beam coupling
Magnetic recording disk having a contiguous fullerene film and a protective overcoat
Carbon fibers and method for their production
Molecular recording/reproducing method and recording medium
Optical photorefractive article
Photorefractive glass article
Method and device for holographic storage
Conductive lubricant for magnetic disk drives
Charge transfer complexes between polyaniline and organic electron acceptors and method of fabrication
Device cathode with extractor grid for display
Epitaxially layered structure
Method and apparatus for cooling GMR heads for magnetic hard disks

Hoechst (main direction: new fullerene compounds)
Intermediates for the preparation of phenylsulfonylurea herbicides and plant growth regulators
Isolation of fullerenes
Carbohydrate-containing polymers, their preparation and use
Metal-fullerene intercalation compounds, process for their preparation and use as catalysts
Aminoureidofullerene and aminothioureidofullerene derivatives and process for the preparation thereof
Process for production of layer element containing at least one monomolecular layer of an amphiphilic molecule and one fullerene
Use of cyclic oligosaccharides as charge control agents
Layer element containing at least one monomolecular layer of a mixture of a fullerene and an amphiphilic molecule
Process for separating fullerenes
Intermediates for the preparation of phenylsulfonylurea herbicides and plant growth regulators
Fullerene derivatives, methods of preparing them and their use
Thermally stable fullerene derivatives

Use of inclusion compounds of cyclic polysaccharides as charge control agents
Highly filled injection moldable polyetherketones

Xerox (main direction: fullerenes in document reproduction)
Liquid ink compositions
Photoconductive imaging members with a fullerene compound
Toner and developer compositions comprising fullerene
Electrophotographic imaging member with overcoatings containing fullerenes
Magnetic fluids and method of preparation
Magnetic materials with single-domain and multidomain crystallites and a method of preparation
Method of manufacturing a donor roll
Ink jettable toner compositions and processes for making and using
Liquid development composition having a colorant comprising a stable dispersion of magnetic particles in an aqueous medium
Process for preparing electroconductive members
Magnetic and nonmagnetic particles and fluid, methods of making and using
Conductive carrier compositions and processes for making and using
Conductive polymer compositions and processes thereof
Magnetic toner and ink jet compositions
Toner composition and processes thereof
Imaging member with partially conductive overcoating

NEC (main direction: electronic devices)
Superconducting material comprising $Rb_xCs_yC_{60}$.
Magnetic recording medium comprising a solid lubrication layer of fullerene carbon having an alkyl or allyl chain
Carbon nanotubule enclosing a foreign material
High-molecular weight carbon material and method of forming the same
Method of producing carbon material by bending at least one carbon atom layer of graphite
Enhanced flux pinning in superconductors by embedding carbon nanotubes with BSCCO materials
Method of purifying carbon nanotubes
Process for purifying, uncapping and chemically modifying carbon nanotubes
Clathrate compounds and processes for production thereof
Graphite filaments having tubular structure and method of forming the same
Carbon material originating from graphite and method of producing same
Cylindrical macromolecule and photometer and magnetometer using the same
Carbon material and method of preparing the same
Solenoid comprising a compound nanotube and magnetic generating apparatus using the compound nanotube

DuPont (main direction: polymers and fibers)
Charge transfer complexes and photoconductive compositions containing fullerenes
Aromatic polyamide compositions and fibers
Fluoroalkylated fullerene compounds
Cyclofluoroalkylated fullerene compounds
Method for introducing a biological substance into a target
Fibers reinforced with inorganic whiskers
Carbon nanostructures encapsulating palladium
Purifaction of pentafluoroethanes
Process for making a field emitter cathode using a particulate field emitter material
Carbon cone and carbon whisker field emitters

The direct fullerenes applications cut across many technology areas. The full impact of fullerenes on the applications areas listed as well as on many other potential applications areas is not reflected in the numbers presented. This is due to the potential added impact from indirect applications. For example, the total impact of fullerenes on health applications (where "health" is one of the patent indicators) would include (1) the direct impact of fullerenes on health (as shown by the indicators), plus (2) the impact of fullerenes on health along the path fullerenes → instruments → health, and (3) the impacts of fullerenes on health along a myriad of other multilink paths as well.

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CI0200117