Patent Analyses of Chemical Protective Clothing Materials

Tun-Min Jai, Dr. Jaw-Hua Chiao

Textiles and Clothing Department, Fu Jen Catholic University, No.510, Jhongjheng Rd., Sinjhuang, Taipei, 242, Taiwan (R.O.C.)

Abstract

This study examined the issued and pre-granted patents of worldwide chemical protective clothing (CPC) materials. The purpose of the study was to combine patent databases and specific chemistry database, SciFinder, to analyze the technological trends and potential commercial CPC material through bibliography and registry number (RN). The conclusions of the study were as follows:

First, in the analysis of patent information, we found that the main international patent classification (IPC) was B32B, layered products. U.S. and German were the leading pioneers in CPC material field. The major assignees were Bluecher, DU PONT and GORE. Each of them had unique technological base.

Secondly, analyzing RN carefully and we found out that the activated carbon, PTFE, and Polyethylene were the main potential commercial CPC materials. After 2000, the activated carbon was integrated with the nanotechnology to promote the adsorption ability as absorption material. On the other hand, the PTFE material was used in membrane to upgrade the air permeability with good resistance to multi-harmful damages. There were many other new CPC materials in the early development stage.

Thirdly, the analytic results showed that key CPC materials concentrated on the barrier ability, adsorption, detoxifying ability, comfort ability, durability, and layer construction. At the same time, the material also integrated into nanotechnology to promote the CPC performances. In the near future, The CPC would be lighter, stronger, and better protected. From passive adsorbent to active detoxifying and combine multi-resistance ability in one piece by applying layer construction to reach the multi-protection purposes, such as protection against nuclear, biological and chemical warfare agents.

Keywords: Chemical Protective Clothing, Material, Patent Analysis, CAS Registry Number, Activated Carbon, PTFE

1. Introduction

1.1 Protective Clothing becomes more and more important

Protection from chemical exposure has been a worldwide long-standing issue for industrial workers and responders to chemical disasters such as wrecks of transporting industrial chemicals (e.g. chloride, fluorine, or sulfuric acid). There are a variety of garments can provide different levels of protection and a long list of agencies involved in developing standards for the workplace.

In 1971, U.S. Occupational Safety & Health Administration (OSHA) established the basic personal protective apparel standard for industry. Therefore, the workers on long time counted on their own devices for defense against the chemical or biological hazards. Later on, NIOSH, NFPA, and various industry safety equipment associations and the first responder groups joined in. The U.S. Anti-Terrorist Act of 1998 appropriated $100 million for the purchase of equipments for fire and police departments of using in response to terrorist acts. Until 2001, the appropriation did not see much use. For the year 2001, about $40 million was spent prior to the attacks of 9/11. Within 2 months of 9/11, another $40 million was issued for the purchase of anti-terrorist equipments. Most of that went toward the purchase of high-level protective garments. In 2002, the Anti-Terrorist Act increased the appropriation from $100 million to $360 million. This money is intended for use on every aspect of anti-terrorist responses, from personnel training to purchasing chemical warfare suits. [3]

1.2 Patent Information as a competitor monitoring and technology assessment

The benefits of patent information for the evaluation of developments in the R&D area have been shown empirically in many studies [1, 2, 8] which goes particularly for innovative and emerging technologies. Observing a company's patent activities in a specific technological field also could be a good method to catch on the company R&D strategy. [5] For example, any sharp increase or decrease on issued and pre-granted patent can be regarded as a change in R&D activity and focus, and may therefore have a technological and commercial impact in the future. Moreover, by using suitable statistics, it can facilitate to identify the leading companies and the assessment of technological distances between competitors. The aim of this paper tried to demonstrate the patent information combining specific database could contribute to the assessment of new material trend and competitive situation among the leading company.

2. Methodology

This study examined the issued and pre-granted patents of worldwide chemical protective clothing (CPC) materials. Patent, as a valuable source of information, the study combined patent databases and specific chemistry database, SciFinder, to analyze the technological trends and potential commercial CPC materials through bibliography and registry number (RN).

The European Patent Office searchable database (esp@cenet®) [4] provided bibliographic data and abstract as well as full text. The International Patent Classification (IPC) had been used as the search criteria to retrieve the research data on CPC material patents. CPC Materials patents are classified under the class number A62D5/00: Composition of materials for coverings or clothing affording protection against harmful chemical agents. Recognizing the multiple filing of patent applications for the same invention in different countries, so called "Patent family", the study just chose one patent from the patent family for avoiding counting repeatedly. The method to carry out this study which made a difference from other traditional patent map analysis was using chemistry database (Scifinder Scholar) and research process. By using Scifinder Scohlar database, the study collected the materials' CAS Registry Number (RN) of CPC and then generated the CPC material trend.

The objectives of this study were as followed:

- finding out the leading pioneers and the most active companies in the field of CPC materials,
- discovering the main CPC materials and their developmental trend,
- establishing the newest material list,
- deriving a proposed construction of future CPC materials from the patent analysis.

The analyzing process of the study was illustrated in Fig.1.

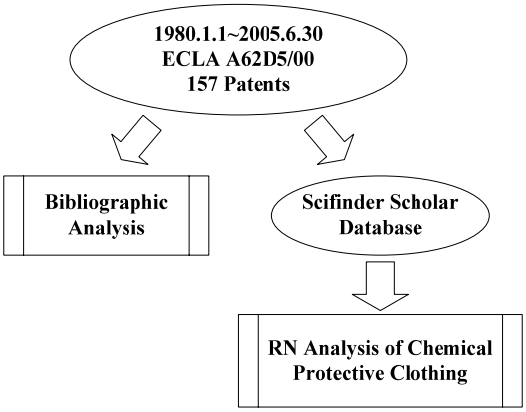

Fig.1. Analysis process of the study

3. Results

3.1 Patent Bibliographic Analysis

3.1.1 Publication Year Analysis

In Fig.2, there was an overview of the CPC material patents development within twenty-five years period. Usually, this field didn't have twenty or more patented technology per year, and there were two major tips within twenty-five years. The 9/11 tragedy in 2001 could be an important reason which caused recent rise on the amount of CPC material patents.

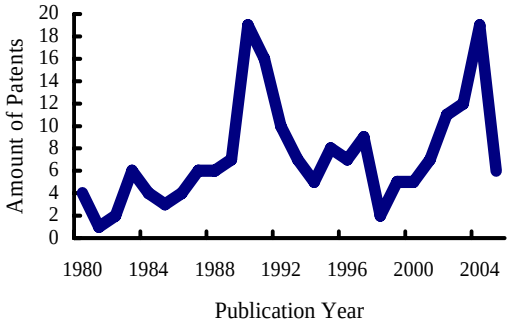

Fig. 2. Publication year analysis

3.1.2 Country Analysis

A total of sixty-six percent patents were registered in United States and Germany (Fig. 3.). Developed Industries with complete regulations of occupational safety and health made US and Germany the biggest markets of CPC.

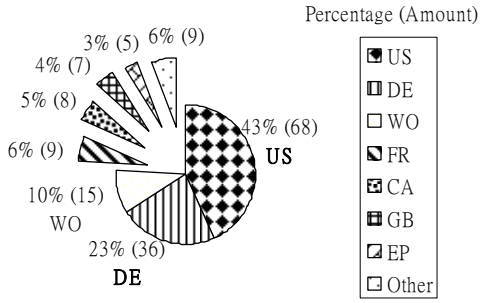

Fig. 3.Country analysis

3.1.3 IPC Analysis

The main International Patent Classifications of CPC were listed in Table 1. We found that the main classifications were focused on A62D5/00 and A62B17/00. The other classes would be used as important cross reference for R&D.

Table 1 Main International Patent Classification (IPC) List

IPC	Definition	Patent Amount
A62D5/00	Composition of materials for coverings or clothing affording protection against harmful chemical agents	54
A62B17/00	Protective clothing affording protection against heat or harmful chemical agents or for use at high altitudes	37
D06N7/00	Flexible sheet materials for wall, floor or like covering materials	16
A41D31/00	Selection of special materials for outerwear	15
A41D13/00	Professional, industrial, or sporting protective garments, e.g. garments affording protection against blows or punches, surgeon's gowns	13
B01J20/28	Solid sorbent compositions or filter aid compositions; Sorbents for chromatography; Processes for preparing, regenerating or reactivating thereof	13
B32B27/12	Layered products essentially comprising synthetic resin next to a fibrous or filamentary layer	12
A41D31/02	Selection of special materials for outerwear of layered materials	11
B32B7/00	Layered products characterized by the relation between layers, i.e. products essentially comprising layers having different physical properties and products characterized by the interconnection of layers	10

3.1.4 Competitors Analysis

Blucher GMBH, E. I. Du Pont de Nemours and Company (Du Pont), and W. L. Gore & Associates (Gore) were the main companies in CPC material field. The IPC analysis pointed out these companies had different developed technologies. Fig.4 showed the graph of main competitors in IPC 3 level analysis. We found that Gore put its effort mainly in the IPC B32B (layered products). Blucher GMBH's CPC material technologies covered IPC B32B, A62D (clothing affording protection against harmful chemical agents), and A41D (protective garments). Fig.5. revealed that Du Pont had equally developed stratagems in IPC A62D5 (composition of materials for coverings or clothing affording protection against harmful chemical agents), A62B17 (protective clothing affording protection against heat or harmful chemical agents) and B32B27 (layered products essentially comprising synthetic resin). Fig.6. illustrated that Bluecher GMBH was dominant in A62D5/00 and A62B17/00. Besides, Bluecher also extended her R&D in D06N7/00 (flexible sheet materials for wall, floor or like covering materials).

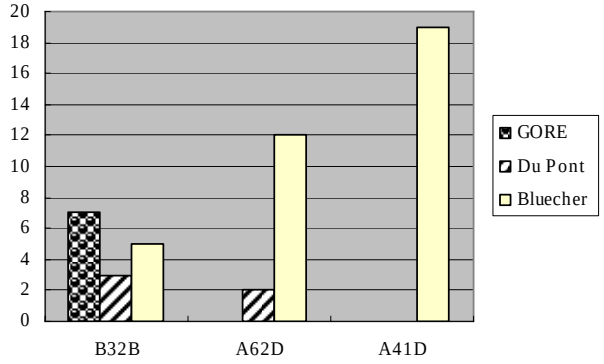

Fig.4. Main Competitors/ IPC 3 level Analysis

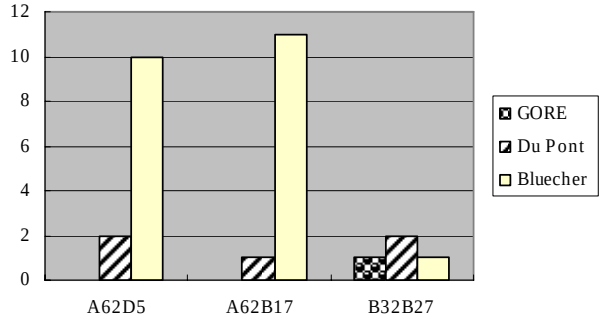

Fig.5. Main Competitors/ IPC 4 level Analysis

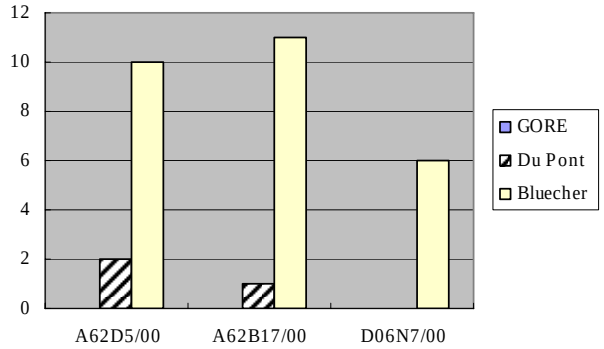

Fig 6.Main Competitors/ IPC 5 level Analysis

3.2 Materials Analysis

3.2.1 CA Registry Number Analysis

There were a variety of materials that could be used to produce chemical protective clothing. However, not all fabrics are usable for every types of garment, and none are all appropriate for use in all chemical handling and/or cleaning up. Materials such as activated carbon, polytetrafluoroethylene (PTFE), polyethylene, had over fifteen percentages. They were traditional but important materials in the manufacturing of chemical protective clothing. The Top 10 CPC materials, their RN and related patent statistics are listed in Table 2.

Table 2. Top 10 materials RN using in CPC

No.	CA Registry Number (RN), Name	Patent Amount	Percentage
1	7440-44-0, Activated carbon,	24	20%
2	9002-84-0, PTFE	18	15%
3	9002-88-4, Polyethylene	18	15%
4	9002-89-5, Poly(vinyl alcohol)	10	8%
5	24937-78-8, Ethylene-vinyl acetate copolymer(EVA)	9	8%
6	25067-34-9, Ethylene-vinyl alcohol copolymer,	9	8%
7	9002-85-1, Poly(vinylidene chloride)	8	7%
8	9003-07-0, Polypropylene	7	6%
9	9010-85-9, 1,3-Butadiene, 2-methyl-, polymer with 2-methyl-1-propene	7	6%
10	7440-22-4, Silver	6	5%

Activated carbon as the dominant one in the CPC materials, it usually used as adsorbent. Since 1988, carbon fibers were used in protective clothing for chemical and biological warfare. In 1990, active carbon was used in moisture-permeable waterproof textile materials for making clean-room suits with adsorbing characteristics. Moreover, in 2002, there was a patent mainly claimed in mass production of nano spherical activated carbon which could increase the adsorbing efficiency substantially. The development of activated carbon is illustrated in Fig.7.

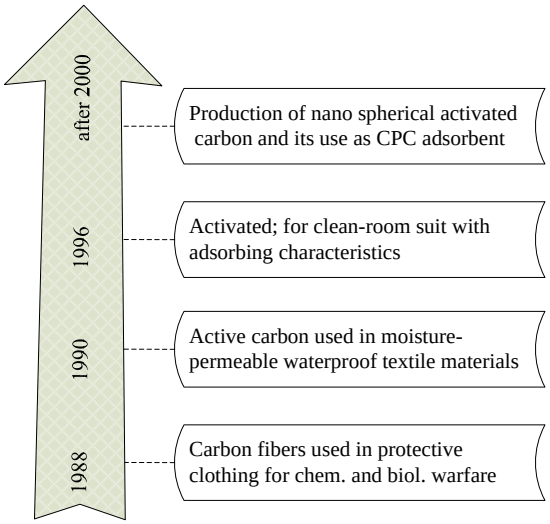

Fig.7 Activated carbon development

After 2000, there were new developments with nano technology in the CPC material R&D. For example, U.S. pre-granted patent 2005101211 claimed that the adsorption layer can be included carbon fibers with diameter of less than approximately 500 nanometers[7]. In a Germany patent, DE10254241, claimed the production of spherical activated carbon having the following pore size distribution: (a) 1.2-1.7 nm: 20-50 %, (b) 1.7-2.1 nm: 20-50 %, (c) 2.1-2.5 nm: 10-25 %, (d) 2.5-2.9 nm: 3-15 %, and (e) 2.9-3.3 nm: 1-10%, whereby the sum of (a) to (e) is 88%. In another Germany patent, DE20306251, the adsorption filtering material (mainly were spherical activated carbon) may contain 0.01-15 wt.% (preferably 5-12%) catalyst from a group of Cu, Cd, Ag, Pt, Pd, Zn, Hg, and their compounds to prevent from breakdown (Table 3).

Table 3. Roles of carbon in patent after 2000

Patent No.	Roles of Carbon Material	Assignees
US2005101211	TEM (Technical or engineered material use); USES (Uses) (fabrics, activated, chem. absorption layer; chem. protective composite substrate and method of producing same)	Univ. Texas Tech. (US)
DE10254241	IMF (Industrial manufacture); NUU (Other use, unclassified); PREP (Preparation); USES (Uses) (spherical activated, adsorbent; prodn. of spherical activated carbon and its use as adsorbent)	RVG Berlin-Brandenburg Ges.Fue. (DE)
DE20306251	TEM (Technical or engineered material use); USES (Uses) (spherical activated; in adsorption filtering material with high adsorptivity and negligible breakdown)	Bluecher GMBH (DE)

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer with numerous applications. Teflon has been the most well known PTFE trademark worldwide since DuPont initially discovered PTFE in 1938. DuPont applied patent for PTFE protective clothing in 1981 with claiming microporous textiles. In 1988, PTFE was used in laminated textiles for chemical, fire, and heat-resistant clothing. Gore coated polyalkyleneimine material on PTFE for absorbing noxious gases in 1992. For enhancing the durability of PTFE, in 1998, there was a patent claimed that coating on one or more sides with a layer of halogen-free thermoplastic olefin resin would made magnitude increases in durability including flex crack resistance, abrasion resistance, and puncture resistance as compared to un-coated fabrics. Until 2003, the Germany patent, DE10354623, claimed the protective clothing could against biological and chemical warfare agents and radioactivity from nuclear explosion. The development of PTFE material was illustrated in Fig.8.

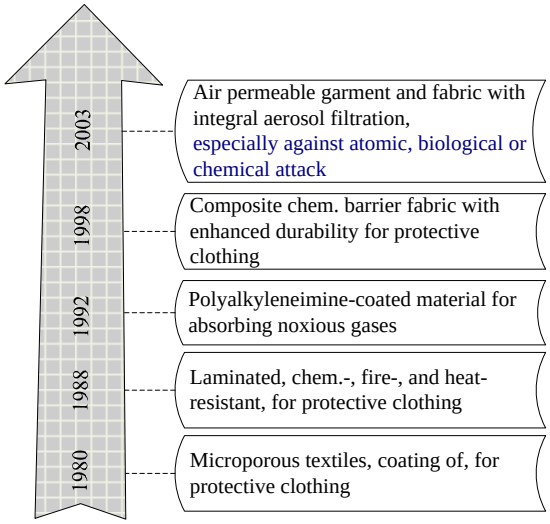

Fig.8. PTFE material development

One protective clothing could against multi-hazards became an important trend in R&D. Thus, PTFE has functioned in CPC patents mainly on adding air permeability and comfort ability with its extremely non-reactive ability (Table 4.).

Table 4.Roles of PTFE Material after 2000

Patent No.	Roles of PTFE Material	Assignees
WO2005002849	PRP (Properties); TEM (Technical or engineered material use); USES (Uses) (manuf. of contamination infiltration barrier films)	Kappler Inc、Langley John Carroll Todd
EP1433394	TEM (Technical or engineered material use); USES (Uses) (membrane; air permeable garment and fabric with integral aerosol filtration)	Donaldson Inc. (US)
DE10354623	TEM (Technical or engineered material use); USES (Uses) (membranes; protective clothing against at., biol. and chem. warfare agents)	Bluecher GMBH (DE)

3.2.2 The newest CPC materials Analysis

CAS has assigned over 25 million registry numbers for chemical substances since 1965. The registry numbers are very useful when searching for a specific chemical substance information. Besides, a registry number allows you to avoid using chemical names, which can vary widely.

A Registry Number (RN) looks like this:

123456-78-9

where the first segment can be from two to six digits long. It is a sequential accession number from the CAS Registry database, and carries no chemical or structural meaning in itself -- it is simply an identification number for a specific substance that CAS has registered. In general, the shorter the first segment, the older the chemical. [6] Therefore, this study selected the materials with six digits in the first segment of RN and listed as below. They could be divided into several sectors, including: absorbent, reactant of spherical activated carbon, barrier layer, flame-retardant agent, modified polymers, dispersant, enhanced durability agent, crosslinking agent, adhesives, polyoxometalate materials for removing environmental contaminant.

Fig 9 showed the new materials for CPC. From this figure, we can trace the R & D of these new materials. Any combination or individual use will be followed carefully.

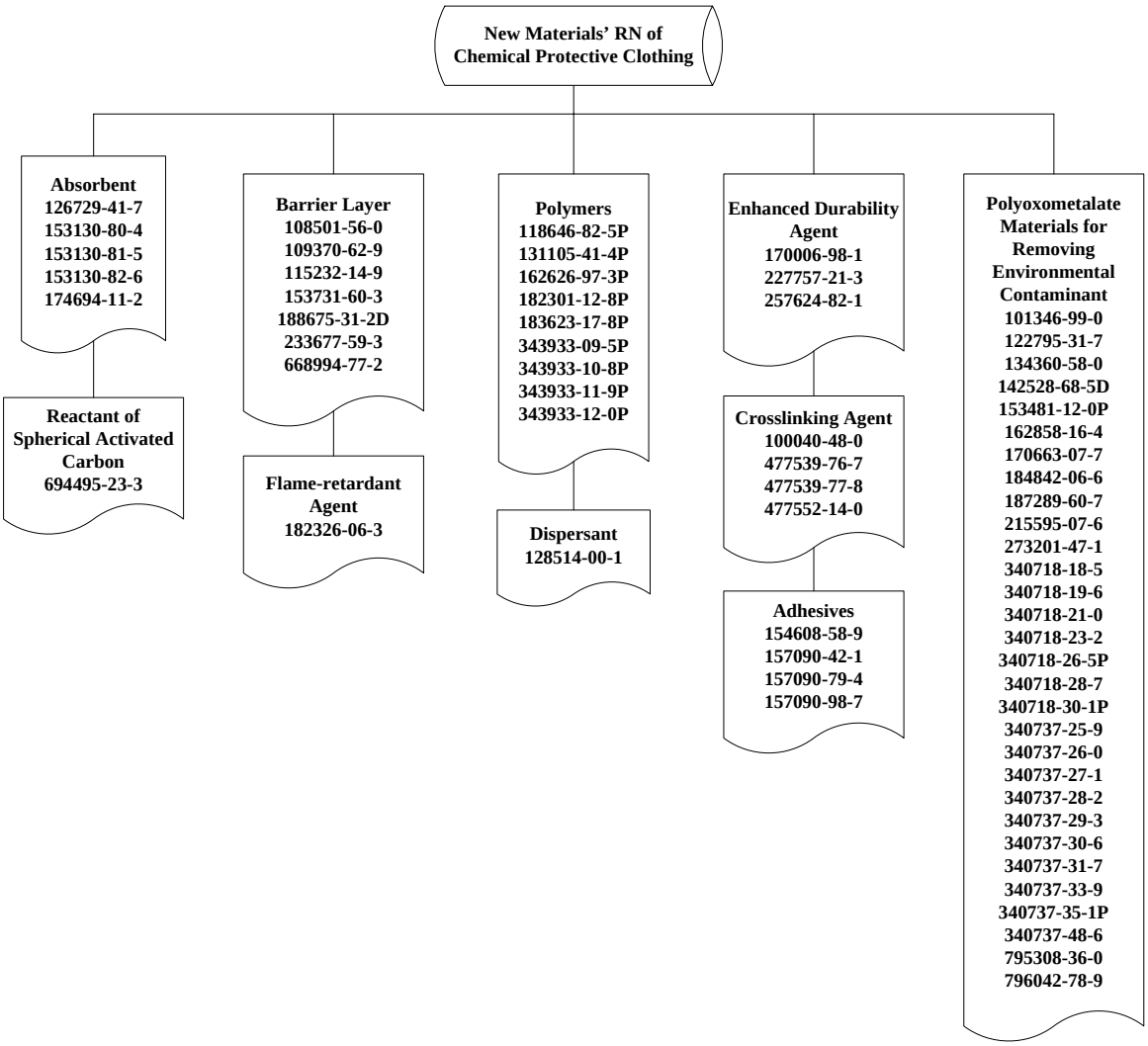

Fig.9. New materials' RN of CP

4. Conclusion

The trend of CPC was using multi-functional layered construction with good durability and comfort ability. (Fig 10) In the near future, The CPC would be lighter, stronger, and better protected. From passive adsorbent to active detoxifying and combining multi-resistance ability in one piece by applying layered construction to reach the multi-protection purposes, such as protection against nuclear, biological and chemical warfare agents.

In this study, we generate a new method to evaluate patent information. With the help of registry number, we could easily collect and analyze material used in a specific technological field. We also can follow every material research, such as mass production and component formulation. It will open a new business world.

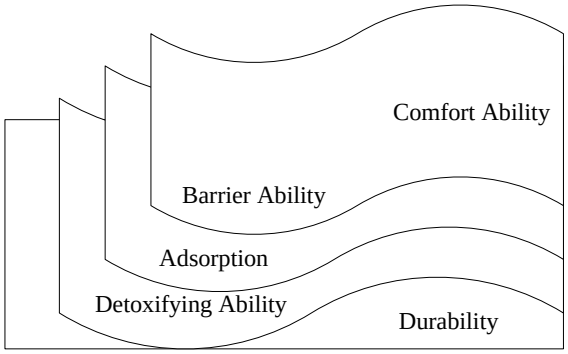

Fig.10. Scheme of layered construction

Acknowledgements

We greatly appreciate our dear family members' and friends' love and encouragement through the whole research process.

References

[1]Chiang, Pi-Ju, Patinformatic study on the development and application of biodegradable fiber technology – polylactic acid fiber and polypropylene terephthalate, Master thesis, Fu Jen Catholic University, 2005

[2]Chiao, Jaw-Hua and Sheng-San Cheng, U.S. patent analysis of textile treatment related to the ultraviolet protection finishes", The 6th Asian Textile Conference, 2001

[3]Crull, Anna W., Protective clothing and gear: body/vehicle armor, fire, chem/bio, Business Opportunity Report GB-142V, Business Communications Company, p.144-145, 2005

[4]European Patent Office, http://ep.espacenet.com/

[5]Fabry, Bernd, Holger Ernst, Jens Langholz, and Martin Koster, Patent portfolio analysis as a useful tool for identifying R&D and business opportunities—an empirical application in the nutrition and health industry, World Patent Information, No. 28, P215-225, 2006

[6]Finding Chemical Abstracts Registry Numbers, www.lib.utexas.edu/chem/info/rn.html

[7]United States Patent and Trademark Office database (USPTO), http://www.uspto.gov/

[8]Wang, Huei-Yu, The development of brand by patent analysis-a case study of Nike Inc., Master thesis, Fu Jen Catholic University, 2003.