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The Requirements of Patentability as Applied to the Chemical Arts

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THE REQUIREMENTS OF PATENTABILITY AS APPLIED TO THE CHEMICAL ARTS

A Thesis

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In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

by
Joy L. Bryant
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APPROVAL SHEET

This thesis is submitted in partial fulfillment of

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DEDICATION

To my family for their support in all of my endeavors.

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The writer would like to express her appreciation to Dr. George Helfrich, Esq., under whose guidance this work was conducted, for his patient guidance and support throughout this program. The author is also indebted to Dr. Dennis Manos, Dr. Robert Orwoll and Dr. Trotter Hardy for their careful reading and criticism of the manuscript.

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ABSTRACT

The purpose of this thesis is to discuss and teach by way of actual examples what is required in order to obtain a patent for an invention relating to the chemical arts.

A patent provides an inventor with the right to exclude others from making, using and selling his invention in the United States in exchange for public disclosure. Patent law is the legal system which provides a means for protecting property in technology. The United States patent system has a long evolutionary history and is constantly subject to change in order to meet the needs of the public.

The patentability of an invention is subject to meeting the requirements set forth in Title 35 of the United States Code (35 U.S.C.). These requirements are both non-technical and technical. The subject matter of the invention must be classified as statutory subject matter (non-technical) and must be novel, useful and nonobvious (technical).

Patent prosecution is the process of obtaining a patent. It is during this process whereby the claims in an application are evaluated in order to determine whether the invention meets the non-technical and technical requirements of patentability.

The individual cases presented show that each case is unique and the strategy which is used in arguing the patentability of an invention differs depending on the facts in the case.

THE REQUIREMENTS OF PATENTABILITY AS APPLIED TO THE CHEMICAL ARTS

THESIS STATEMENT AND OVERVIEW

The purpose of this thesis is to discuss and teach by way of actual examples what is required in order to obtain a patent for an invention relating to the chemical arts. In Chapter 1, a historical review is given which describes the evolution of the United States patent system. In Chapter 2, the requirements of patentability are addressed. A general overview of the substance of patent law as it relates to patentability is provided. In Chapter 3, a brief description of the process of obtaining a patent (patent prosecution) is given and the prosecution history is provided for several cases. By reading these cases, the reader will see how the requirements for patentability are argued and met for inventions relating to the chemical arts.

CHAPTER I

Historical Review

A patent is both a legal and a scientific document containing new technology. It affords the inventor a way to protect his technology and also acts as a mechanism whereby technological advances are promoted in society. Patent law is the legal system which provides a means for protecting property in technology. The development of the patent system has a long evolutionary history.

In the fourth century B.C., the first reference to patents was recorded by Aristotle in his book "Politics". He writes of Hippodamus of Miletos, who proposed a system of rewards for those who discover things useful to the state. It is this very proposal which introduces several themes found in patent law today. Hippodamus' reasoning towards solving issues followed a "problem-solving" approach, which was a result of his technical training. This type of approach has been key to the evolution of patent law. Moreover, Hippodamus' proposal to reward the inventors of useful things is the underlying principle of all patent systems.

The next reference to a patent structure is found in the Renaissance period. Historians suggest that the renewed focus on the importance of the individual was the key intellectual change of the Renaissance. This emphasis provided an environment in which patent systems could begin to emerge and thrive.

In the late fifteenth century, the first administrative means for granting patents appeared in Venice. The term patent originated during this period and came from the Latin word "patere" which means "to be open". This word refers to an open letter of privilege from the sovereign. The practice of granting patents became more customary after the Venetian Senate's 1474 Act. This Act reads:

> Be it enacted that, by the authority of this Council, every person who shall build any new and ingenious device in this City, not previously made in this Commonwealth, shall give notice of it to the office of our General Welfare Board when it has been reduced to perfection so that it can be used and operated. It being forbidden to every other person in any of our territories and towns to make any further device conforming with and similar to said one, without the consent and license of the author, for the term of 10 years. And if anybody builds it in violation hereof, the aforesaid author and inventor shall be entitled to have him summoned before any Magistrate of this City, by which Magistrate the said infringer shall be constrained to pay him one hundred ducats; and the device shall be destroyed at once.[1]

All of the essential characteristics of the present day patent statute are contained in the Venetian Act. The act protects "devices"; states that they must be registered with a specific agency; says that they must be "new and useful", "reduced to perfection," and "not previously made in this Commonwealth"; provides a fixed term of ten years; and sets forth a procedure to determine infringement, as well as a remedy.[2]

When trade opened in Europe, sometime during the middle of the sixteenth century, the Venetian concept spread. It was the Italian craftsmen who brought with them the idea of legal protection for inventions. Patents were used as a mechanism to lure foreign inventors who would introduce continental technologies into England. However, by the mid-eighteenth century, instead of the technology flow going into Britain it began to flow to its overseas rivals, including the American colonies.[3]

In the early seventeenth century, patents became more of a royal favor, which displeased the members of Parliament. This lead to the Statute of Monopolies of 1624. This statute allowed for a review of all privileges granted by the crown and eliminated all of those which were not based on true inventions. However, even with this statute in effect, the British patent system remained a largely informal administrative apparatus and influence in the royal court still proved to be beneficial in obtaining a patent.

The Industrial Revolution provided an opportunity to generate a new interest in patents. A new change was implemented into the system which required the applicant to describe his or her invention clearly and completely. This change was a result of the 1778 opinion of Judge Mansfield in *Liardet v Johnson.*[4] This description requirement was to benefit society by providing the technological know-how for the invention and signified the introduction of new and useful information to the technical arts.

Patents were introduced to the American colonies between 1640 and 1776, with the individual states having the authority to grant the patent. However, conflicts began to arise concerning who the actual inventor was for some of the technologies. In order to resolve this problem, the Constitutional Convention of 1789 came forth with the provision of Article I, Section 8, which authorized Congress to provide exclusive rights for a limited time to authors and inventors "for their respective writings and discoveries". Thus, a national patent system was developed which had a basis in the Constitution itself. The first U.S. patent statute was passed in May, 1790[5] with the first patent issuing shortly thereafter to Samuel Hopkins for his process for making potash from wood ashes.

Although Thomas Jefferson was the author of the Constitutional provision and a contributor to the original statute, the patent system did not reach its full proportion until it was revised in 1836. In this revision, an examination system replaced a registration system which had itself been substituted in 1793 for the original 1790 procedure.

As greater demands were placed on the patent system, new rules were developed. The requirement of "invention" in addition to novelty and utility is just one example of a new rule. This requirement was developed in the mid-nineteenth century to help limit the number of issued patents. It was late in the nineteenth century that the patent structure began to evolve to its present form.

As industry grew and research and development groups began to appear in large businesses, patents were used to measure productivity and served to justify the business' importance. Unfortunately, during the 1920's and 1930's, the growth of the antitrust movement resulted in an increased focus on patents, which were viewed as weapons for big businesses. This led to an anti-patent movement of which the central idea was that the rights of powerful corporations had come to dominate the interests of the community.

The attacks on the patent system ended with the attack on Pearl Harbor. The demands of the war called on scientists to provide a vast array of technologies in a very short time. By the time the war ended, the anti-patent movement had calmed down. The 1952 Patent Act was passed which provided the first major revision of the patent code since the nineteenth century. This act restated many of the fundamental principles which provide the basis for the American patent system.

Unfortunately, much of the anti-patent sentiment of the 1930s could still be found in the courts. This sentiment was supported by the anti-technology thinking of the 1960s and early 1970s. It was during this time that industry downplayed the importance of patents. It was difficult to get a patent upheld in many federal circuit courts and the doctrine and basic attitudes of the circuits concerning patents were very diverse. Because of this diversification, the idea was proposed to have a single, unified court of appeals specifically designated for patent cases. This idea underwent much debate throughout the 1970's.

In 1982, Congress passed the Federal Courts Improvement Act, which created the new Court of Appeals for the Federal Circuit (CAFC) with the aim at unifying the patent doctrine. One of the primary functions of this court is to hear all appeals from the federal district courts involving patents. The formation of the CAFC has greatly enhanced the structure of the patent system. Patents are more likely to be held valid and it is much easier to get an injunction against an infringer.

It is evident from the historical review that the United States patent system is constantly undergoing changes to meet the needs of the public. One proposal which is currently being discussed in the patent office involves changing the system from a first-to-invent system to that of a first-to-file system. Another proposal that is also under consideration is to publish all patent applications 18 months after the filing date and to extend the period of the patent grant from 17 years to 20 years (for utility patents). Both of these proposals would cause the U.S. patent system to parallel foreign patent systems. Who knows what the next decade will bring?

In the next chapter, the substance of patent law with respect to the requirements of patentability will be discussed.

Notes for Chapter I

1. Mandich, *Venetian Patents (1450-1550)*, 30 J. Pat. Off. Soc'y 166, 177 (1948).
2. R.P. Merges, Patent Law and Policy, (Charlottesville, 1992), 4.
3. W. Hamilton, The politics of Industry 68 (1957).
4. Merges, p. 5.
5. Patent Act of 1790, Ch. 7, 1 Stat. 109-112 (April 10, 1790).

CHAPTER II

Requirements of Patentability

A. Statutory Subject Matter

In order for an invention to be patented, its subject matter must meet the requirements of patentability presented in Title 35 of the United States Code (35 U.S.C.). It is important to note that not all inventions or discoveries are patentable. Patentable subject matter is classified into one of three statutory classes which define the type of invention. A utility invention is defined in 35 U.S.C. §101 as a machine, an article of maufacture, a composition of matter or a process. Design inventions are described in 35 U.S.C. §171 as an ornamental design for an article of manufacture. Lastly, inventions which are for botanic plants are defined in 35 U.S.C. §161.

Non-patentable or non-statutory subject matter identifies that which is not patentable. Examples of non-statutory subject matter include: (1)that which is explicitly excluded by statute; (2) that which existed and was previously unknown or unappreciated such as principles or laws of nature and naturally occurring articles; and (3) that which requires only mental activity such as printed matter, methods of doing business and mental processes. One possible way to protect non-statutory subject matter may be through copyright, which will not be discussed in this thesis.

B. Technical Requirements of Patentability

Once the subject matter of an invention is found to qualify as statutory subject matter, it must meet the technical requirements of patentability. These requirements are defined as: novelty[1], utility[2] and nonobviousness[3], each of which must be found in a claim for an invention to be patentable.

1. Novelty

The novelty of an invention is determined both subjectively and objectively. The subjective position which is implicit in every novelty determination is the frame of reference, "New to whom?". "How much of a difference and what kinds of differences make a thing new?" is the question encompassed by the objective determination of novelty. To answer these questions, a comparison is made between the invention and the prior art.

Prior art exists as the fund of information which is available or accessible to the public prior to and at the time of the invention. Relevant prior art is considered as that to which one can reasonably be expected to look to for a solution to the problem that the patented device attempts to solve. For example, if an inventor wishes to develop a new polyimide for space applications, he would not look to pharmaceutical technology. In addition, if something disclosed in the prior art is substantially identical to the claimed invention, the invention is considered to be "anticipated" by the art which negates the novelty of the invention.

Novelty suggests change or innovation: a difference between that which is sought to be patented and that which came before (prior art). It has been said to be the essence of and key requirement for patentability. The requirement for novelty or nonanticipation is defined in 35 U.S.C. §102. Section 102 sets forth the types of activity which negate novelty.

a. 35 U.S.C. §102(a)

According to 35 U.S.C. §102(a): "A person shall be entitled to a patent unless - the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for patent." For something to constitute prior art under 35 U.S.C. §102(a), it must be known to or used (not the same as patented or published) by others in the United States, not anywhere in the world, prior to the invention. The reasons for this are that (1) such information is not accessible to U.S. industry and (2) proving its very existence would be difficult. Conversely, if a patent or published document occurs anywhere in the world prior to the invention, it is considered prior art and precludes patenting of the invention. The fact that an inventor was unaware of the prior art is immaterial. Thus, if there is a physical (or chemical) identity between the prior art and that sought to be patented, that which is sought to be patented is said to be anticipated by the prior art.

The definition of a publication is exemplified in the case of *Jockmus v. Leviton*, 28 F.2d 812 (2d Cir. 1928), where the court agreed that a catalog distributed generally to a trade is a publication.

> [Plaintiff, holder of a patent on an adjustable lightbulb holder in the shape of a candle, sued defendant for infringement. Defendant asserted lack of novelty, in that plaintiff's invention was anticipated by a product pictured in a commercial

catalogue distributed to French customers of a German firm. From a judgment of validity and infringement, defendant appeals.][4]

U.S. Circuit Judge L. Hand writes:...A single copy in a library, though more permanent is far less fitted to inform the craft than a catalogue freely circulated, however ephemeral its existence; for the catalogue goes direct to those whose interests make them likely to observe and remember whatever it may contain that is new and useful.

b. <u>35 U.S.C. §102(b)</u>

Another printed publication provision of the statute is set forth in 35 U.S.C. §102(b) which reads: "A person shall be entitled to a patent unless - the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States." What constitutes a printed publication within the meaning of 35 U.S.C. §102(b) is not entirely agreed upon. If the information has been reproduced or duplicated and has been made available to the extent that persons interested and ordinarily skilled in the art, exercising reasonable diligence, can locate it and recognize and comprehend the essentials of the claimed invention from it without the need of further research or experimentation, it may be said that the information exists in a printed publication.[5] Public accessibility of a printed document determines whether a printed document constitutes a bar (or denies patentability) under 35 U.S.C. §102(b). The key factor is not access by a specific segment of the public, or number of persons, or even by any specific means, but simply distribution of the document to any segment of the public.

In *In re Hall*, 781 F.2d 897, 228 U.S.P.Q. (BNA) 453 (Fed. Cir. 1986), the issue discussed is whether a doctoral thesis is available as a printed publication. The Federal Circuit stated :

> The [printed publication] bar is grounded on the principle that once an invention is in the public domain, it is no longer patentable by anyone.
>
> The statutory phrase "printed publication" has been interpreted to give effect to ongoing advances in the technologies of data storage, retrieval, and dissemination. Because there are many ways in which a reference may be disseminated to the interested public, "public accessibility" has been called the touchstone in determining whether a reference constitutes a "printed publication" bar under 35 U.S.C. §102(b). ...The proponent of the publication bar must show that prior to the critical date the reference was sufficiently accessible, at least to the public interested in the art, so that such a one by examining the reference could make the claimed invention without further research or experimentation. (Explanation supplied.)

The court agreed with the board that the thesis was available as a printed publication based on the evidence of the general library practice which was relied upon to establish an approximate time when the thesis became available.

Under §102(b) a patent is barred if the invention was patented, published, publicly used or sold in the U.S. more than one year prior to the date of the application, regardless of who was responsible for it. In other words, the inventor's own acts can keep him from patenting. This is in contrast to §102(a) where one's own invention, whatever the form of public disclosure, is not prior art against one's application for patent. The activities of §102(a) must be committed by others before the applicant's invention. In §102(b), anyone's actions, including the inventor's, more than one year prior to his filing of the application may constitute a statutory bar.

In *UMC Electronics Co. v. United States*, 816 F.2d 647; 2 U.S.P.Q.2d (BNA) 1465 (Fed. Cir. 1987), the Federal Circuit held that a reduction to practice of the claimed invention is not an absolute requirement of the on-sale bar within the meaning of 35 U.S.C. §102(b). In this case, UMC had made an offer to sell their later patented UMC-B accelerometer to the Navy more than one year prior to the filing date of the application. UMC took the position that when they made the offer of sale, their invention, UMC-B, had not been reduced to practice in the interference sense. The Federal Circuit stated:

> Under 35 U.S.C. §102(b), the commercial exploitation and the state of development of the invention one year before the filing of the application for the subject invention are critical to resolution of the on-sale issue. The Claims Court analyzed the on-sale bar under the following three-part test: (1) The complete invention claimed must have been embodied in or obvious in view of the thing offered for sale; (2) The invention must have been tested sufficiently to verify that it is operable and commercially marketable; and (3) Finally, the sale must be primarily for profit rather than for experimental purposes. [The trial court had found a reduction to practice (element (2)), but no physical embodiment of the invention in the thing offered for sale (element (1)). The Federal Circuit found this inconsistent, and concluded that there had not in fact been a reduction to practice.

> Having so concluded, the court turned to the question whether this by itself removed UMC from the effects of the §102(b) on-sale bar.]
>
> The court concluded that reduction to practice of the claimed invention has not been and should not be made an absolute requirement of the on-sale bar. However, they did make an exception for experimental use, stating that if the inventor had merely a conception or was working towards development of that conception, it can be said there is not yet any "invention" which could be placed on sale. A sale made because the purchaser was participating in experimental testing creates no on-sale bar...UMC admits that the offer it made was for profit, not to conduct experiments. (Explanation supplied.)

In some instances, an inventor may publicly disclose his invention less than one year prior to the filing of his application. This gives rise to a prior art reference which is not a statutory bar. However, if the invention is disclosed by another less than one year prior to the application filing date, either the reference must be argued over or it may be removed by filing an affidavit or declaration satisfying the requirements of Title 37 of the Code of Federal Regulations section 1.131 (37 C.F.R. §1.131).

c. 35 U.S.C. §102(c)

Section 102(c) applies when the inventor has abandoned his invention. It reads: "A person shall be entitled to a patent unless - he has abandoned the invention". Thus, if the inventor has abandoned the invention, he is precluded from obtaining a valid patent subsequent to that abandonment. Abandonment means that the original inventor has voluntarily terminated any effort to exploit the invention. It is not the same as abandoning an application for patent. Abandonment may occur if a patentee discloses an invention in his issued patent but does not claim it. Abandonment can also occur if the inventor states in a notebook that the invention, upon actual reduction to practice, does not satisfy the objectives. (Actual reduction to practice occurs at the time the invention is made in its fully operable form.) In some instances, an inventor may regain his right to a patent if he proceeds diligently towards obtaining a U.S. patent.

d. 35 U.S.C. §102(d)

No U.S. patent may validily issue for an invention which had been filed as a foreign application more than twelve months before the U.S. filing date and has issued as a patent at any time before the actual filing in the U.S.. This is stated in 35 U.S.C. §102(d) where: "A person shall be entitled to a patent unless - the invention was first patented or caused to be patented,...by the applicant or his legal representatives or assigns in a foreign country prior to the date of the application for patent in this country on an application for patent or inventor's certificate filed more than twelve months before the filing of the application in the United States." Section 102(d) evolved in stages from section 25 of the Patent Act of July 8, 1870 which limited the term of a U.S. patent on any invention first patented in a foreign country to the earliest date of expiration of any foreign patent(s). The U.S. became a member of the Paris convention in 1887. Five years later, Congress amended section 25 to make its prohibition applicable only to patent applications which were filed in the U.S. more than twelve months after the filing of the application abroad. Therefore, two requirements must be met in order to deny patentability: (1) the application for the same invention must be filed in a foreign country more than 12 months before filing in the U.S.; and (2) the foreign patent must issue before filing the U.S. application.

e. 35 U.S.C. §102(e)

Section 102(e) states: "A person shall be entitled to a patent unless - the invention was described in a patent granted on an application for patent by another filed in the United States before the invention thereof by the applicant for patent, or on an international application by another who has fulfilled the requirements of paragraphs (1), (2), and (4) of section 371(c) of this title before the invention thereof by the applicant for patent." This section is a codification of the Supreme Court case, *Alexander Milburn Co. v Davis-Bournonville Co.*, 270 U.S. 390 (1926), which held that a U.S. patent is effective as a reference against a subsequently filed U.S. patent application of another as of its filing date, and not as of the date that it issued as a patent. It provides an exception to the general rule that prior art knowledge must be public in order to defeat another's patent rights. Thus, secret prior art arises as a result of the content of a U.S. patent application being unavailable to the public until the patent has issued. The Supreme Court was of the opinion that administrative delays in the Patent Office should not detract from the anticipatory effect of what has actually been done. The effective date of a U.S. patent as a reference under §102(e) is its filing date. However, if an application never matures into an issued patent, it cannot be used as prior art unless it is incorporated by reference into an issued U.S. patent.

f. 35 U.S.C. §102(f)

Section 102(f) sets forth that the applicant must be the inventor. It states: "A person shall be entitled to a patent unless - he did not himself invent the subject matter sought to be patented." This section defines the inventor as the one who conceives the claimed invention in its complete and operative form, and is applicable where an applicant has derived the invention from another. This rule is employed if the applicant learned about the invention from the first inventor and then filed an application for the invention.

g. 35 U.S.C. §102(g)

An interference occurs when either two applications or an application and an issued patent claim the same invention. It is the responsibility of the patent office to determine who is entitled to the invention based on the earliest date of invention (priority). In order to determine priority of invention, the provisions of the second sentence of
35 U.S.C. 102(g) are utilized which states:

> A person shall be entitled to a patent unless - before the applicant's invention thereof the invention was made in this country by another who had not abandoned, suppressed, or concealed it. In determining priority of invention there shall be considered not only the respective dates of conception and reduction to practice of the invention, but also the reasonable diligence of one who was first to conceive and last to reduce to practice, from a time prior to conception by the other.

In this particular instance, the prior art exists in the form of someone other than the applicant making the applicant's claimed invention in the U.S. prior to the applicant's own date of invention. 35 U.S.C. §102(g) differs from section 102(a) where the invention had to be used by more than one person. If the person who is not the applicant abandons, suppresses or conceals his invention, the effect of his invention as prior art is lost under §102(g). This section not only serves as the basis for an interference but it may also form the basis of a defense in a suit for patent infringement.

Table I summarizes the various acts which prohibit novelty and constitute statutory bars under 35 U.S.C. §102 and prevent the issuance of a patent to an inventor for his invention.

2. Utility

In addition to an invention being novel, it also must be useful. This requirement is set forth for utility inventions in 35 U.S.C. §101, which states: "Whoever invents or discovers any new and useful process, machine, manufacture, or composition of matter, or any new and useful improvement thereof, may obtain a patent therefor, subject to the conditions and requirements of this title." (emphasis added) In order to satisfy the utility requirement of 35 U.S.C. §101, a significant use for the claimed invention must exist. Paragraph one of 35 U.S.C. §112 incorporates section 101 into it by stating "The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention." The term "useful" is simply defined as operative and is understood within 35 U.S.C. §112. That is, the invention must have some potentially

TABLE I

ACTS PROHIBITING NOVELTY AND CONSTITUTING STATUTORY BARS UNDER 35 U.S.C. §102[6]

Section of 35 U.S.C. 102	ACTS IN THE UNITED STATES		ACTS IN FOREIGN COUNTRIES
	IF AT ANY TIME BEFORE DATE OF HIS INVENTION THE INVENTION WAS		
(a) 1.	Known or used by others.	1.	Does not apply.
(g) 2.	Invention made by another who has not suppressed or concealed it.	2.	Does not apply.
(e) 3.	Filing by another person of a U.S. Patent application on which a U.S. Patent issues disclosing the invention.	3.	Does not apply.
(a) 4.	Patented or described in a printed publication.	4.	Patented or described in a printed publication.
	IF ONE YEAR OR MORE BEFORE FILING OF HIS US APPLICATION THE INVENTION WAS		
(b) 5.	Patented or described in a printed publication.	5.	Patented or described in a printed publication.
(b) 6.	Public use or sale.	6.	Does not apply.
	ANY TIME BEFORE FILING HIS US APPLICATION		
(c) 7.	Abandoned his invention.	7.	Abandoned his invention.
(d) 8.	Does not apply.	8.	Inventor's own (or legal) representatives or assigns) foreign patent issues prior to U.S. filing date based on a foreign patent application filed more than 12 months prior to the corresponding U.S. application.
(f) 9.	Did not himself invent subject matter sought to be patented.	9.	Did not himself invent subject matter sought to be patented.

beneficial use. Therefore, in order to meet the utility requirement, a patent must provideand claim an invention which is operative for a purpose which is set forth in the patent.

The utility requirement sometimes presents a problem for certain chemical inventions where a new compound has been prepared but the specific use of the compound remains unknown. This occurs when a chemist is exploring a general class of compounds which have a unique set of properties. In *Brenner v. Manson*, 383 U.S. 519, 148 U.S.P.Q. (BNA) 689 (1966), the issue of utility was addressed for a chemical process. In particular, the questions of whether a chemical process was useful within the meaning of 35 U.S.C. §101 either (1) because it works or (2) because the compound which is the product of the process belongs to a certain class of compounds. The Patent Office examiner had rejected the application for failure "to disclose any utility for" the chemical compound produced by the process. The applicant, Manson, presented an article showing a use for the class of compounds which included the compound in question. The Board of Appeals stated, "It is our view that the statutory requirement of usefulness of a product cannot be presumed merely because it happens to be closely related to another compound which is known to be useful." The Court of Customs and Patent Appeals (CCPA) reversed, stating "where a claimed process produces a known product it is not necessary to show utility for the product," so long as the product "is not alleged to be detrimental to the public interest." The Supreme Court reversed the judgement of the CCPA, stating that utility for a process is not shown until utility of the product from the process is shown even if it is the process which is claimed as the invention.

3. Nonobviousness

The last requirement for patentability is that of nonobviousness and is set forth in 35 U.S.C. §103, which states:

> A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.
>
> Subject matter developed by another person which qualifies as prior art only under subsection (f) or (g) of section 102 of this title shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

a. The Relationship of Nonobviousness to Anticipation

Nonobviousness is a broader, more general condition of patentability and is related to anticipation. If a patent claim is found to be invalid due to anticipation under 35 U.S.C. §102, it would also be considered invalid because of obviousness under 35 U.S.C. §103. In addition, it superimposes the requirement that the claimed invention as a whole must also have been nonobvious "at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains".[7]

b. Guidelines for Nonobviousness

Prior to the passage of section 103, patentability was based on "the level or standard of invention".[8] Under this subjective standard, each judge was required to determine whether a particular contribution to science or technology was sufficiently different from the prior art to constitute a level of invention deemed worthy of being considered an invention. There was a problem with this test in that the judges tended to phrase the test differently and apply it inconsistently. In 1952, section 103 was passed to substitute nonobviousness for the subjective "standard or level of invention". However, it was unclear as to whether the new Act simply re-stated pre-1952 law or actually changed it. In 1966, the Supreme Court provided new guidelines for nonobviousness in their ruling in the patent Trilogy, i.e., *Graham v John Deere Co.*, 383 U.S. 1, 148 U.S.P.Q. 459 (1966); *Calmar & Colgate-Palmolive Co. v Cook Chemical Co.*, 383 U.S. 1, 148 U.S.P.Q. 459 (1966); and *United States v Adams*, 383 U.S. 39, 148 U.S.P.Q. 479 (1966). According to these guidelines, the obviousness or nonobviousness of the invention is determined by: (1) the scope and content of the prior art; (2) the differences between the prior art and the claims in issue; and (3) the level of ordinary skill in the pertinent art.

c. Prior Art and Nonobviousness

The question of obviousness is difficult to answer. The difficulty in answering this question is due in no small part to the strong temptation to resort to and rely on hindsight in formulating the answer. It is improper to use the patent application as a guide through the prior art references, combining the right references in the right way to arrive at the result of the claims involved. Obviousness cannot be established by combining the teachings of the prior art to produce the claimed invention without some teaching, suggestion or incentive which supports the combination. A patentable invention may reside in the discovery of the source of a problem even though the remedy may be obvious once the source of the problem is identified. In the case of a chemical invention, determining whether or not a novel chemical structure is obvious requires consideration of the properties of the structure and the problem it solves, viewed in light of the teachings of the prior art. In the analysis of obviousness, it is the magnitude of the differences rather than their existence which dictates the conclusion. Moreover, discovery and recitation of an additional advantage associated with doing what the prior art suggests does not lend patentability to an otherwise unpatentable invention.

d. Obvious Modifications

Often, an inventor will change the amount or relative proportions of the constituents of a composition of matter to achieve his final result. This is ordinarily considered to be an obvious modification. In the same way, the omission of an ingredient of a composition of matter with only the corresponding loss of the omitted component's properties can fairly be said to be obvious. Similarly, the mere substitution of one material, albeit superior, for another is ordinarily deemed to be obvious.[9]

e. Frame of Reference

Under 35 U.S.C. §103, the frame of reference is a person having ordinary skill in the pertinent art. Such a person is one who thinks along the line of conventional wisdom in the art and is not one who undertakes to innovate, whether by patient and often expensive, systematic research or by extraordinary insights. The actual inventor's skill is irrelevant to the inquiry as to whether an invention is obvious. Furthermore, a reference may be applicable as prior art if its teachings place it within the field of the inventor's endeavor or, alternatively, within a field reasonably related to the particular problem with which the invention addresses.

f. Prima Facie Obviousness

A prima facie case of obviousness is established where the teachings of the prior art appear to suggest the claimed subject matter to persons of ordinary skill in the art. Once a prima facie case has been established by the Patent and Trademark Office (PTO), it is the applicant's responsibility to provide objective evidence which shows that the invention is not obvious. Once this evidence has been submitted, it must be considered anew. The entire path which was followed to arrive at the original decision of obviousness must be retraced in order to determine whether the applicant's burden of going forward to rebut a prima facie case of obviousness has been successfully accomplished. Facts established by rebuttal evidence must be evaluated with facts on which the conclusion of prima facie obviousness was reached, and not against the earlier conclusion itself.

To make a prima facie case of obviousness against a new chemical compound, the prior art need only show a structurally similar compound and give reasons or motivation to make the claimed compound.[10] Results which are truly unexpected, unusual, or surpassing may render the invention as a whole unobvious, regardless of how little its structure differs from the prior art, so long as there is some actual physical difference. While a chemical compound is not obvious unless its structure is obvious, its patentability is not to be determined solely on the basis of structural obviousness or prima facie obviousness. One who claims a compound that is structurally similar to a prior art compound must rebut the presumed expectation that structurally similar compounds have similar properties. An unexpected property possessed by the new compound would be evidence of its nonobviousness. Another way to overcome obviousness is to show an unexpected increase in the activity of a structurally obvious compound. "A compound and all of its properties are inseparable; they are one and the same thing...But a formula is not a compound and while it may serve in a claim to identify what is being patented,...the thing that is patented is not the formula but the compound identified by it."[11] Thus, the application of 35 U.S.C. §103 to the subject matter as a whole must be considered.

g. Obvious to Try

Scientists will often pursue an experimental path based on their past experiences aspiring to obtain a particular result. This would be considered as "obvious to try" and is not the same as obvious under 35 U.S.C. §103. Simply because a certain approach might be "obvious to try", does not render the invention unpatentable if upon trial, it is found that the approach yields a truly unexpected result. Alternatively, doing what the prior art references try to avoid is completely the opposite of obviousness.

h. Secondary Considerations

Also to be considered in evaluating unobviousness are the so-called subtests of invention or secondary considerations. These include evidence of the skepticism of experts; that the claimed innovation met with commercial success; that the invention satisfied a long-felt need; or that the invention met with commercial acquiescence. These subtests amount to circumstantial evidence of unobviousness. However, it is important to realize that a secondary consideration may not alone satisfy the requirement of nonobviousness. These considerations are objective criteria of obviousness that help illuminate the subjective determination involved in drawing the legal conclusion of obviousness. The link between commercial success and unobviousness is only indirect and inferential. However, likelihood of commercial success is not a requisite of patentability and is not to be equated with unobviousness. An invention may be truly unobvious and patentable and yet not be commercially feasible. The failure of others to provide a feasible solution to a long-standing problem is supportive of nonobviousness. A showing of long-felt need coupled with a showing of commercial success are indirect but relevant evidence of unobviousness. Long-felt demand tends to establish unobviousness while prompt inventions, once the need becomes apparent, tend to establish obviousness. Commercial acquiescence looks to the actions or inaction of competitors in regard to the patent in issue. The willingness of competitors to take a license or their efforts to design around or otherwise avoid its claims may serve as an unspoken recognition by them of the patent's validity and, hence, provide circumstantial evidence of the unobviousness of the innovation. Lastly, evidence that experts in the art believe that the result achieved or the means or steps by which a result is achieved is not possible or feasible is taken as circumstantial evidence of the nonobviousness of what is achieved.

i. Nonobviousness for Chemical Inventions

The entire development of nonobviousness for chemical inventions is summarized in the single case, *In re Dillon*, 919 F.2d 688, 16 U.S.P.Q.2d 1897 (Fed. Cir. 1990), *cert. denied*, 111 S. Ct. 1682 (1991). Therein the Federal Circuit said:

> [The claimed invention in this case relates to certain fuel compositions with a major component of a gasoline and a minor component of a tri- or tetra-orthoester that reduces soot emissions when the fuel is burned.] The composition claims were rejected as obvious under 35 U.S.C. §103 over two primary references - Sweeney U.S. patents 4,390,417 ('417) and 4,395,267 ('267) - in view of secondary references including Elliott U.S. patent 3,903,006 and Howk U.S. Patent 2,840,613. Sweeney ('417) discloses tri-orthoesters for dewatering fuel. Elliott equates tri-orthoesters and tetra-orthoesters as water scavengers in hydraulic fluids. Howk equates tri- and tetra-orthoesters in a similar type of chemical reaction. The Board stated that the Elliott reference shows equivalence between tetra-orthoesters and tri-orthoesters, and that "it is clear from the combined teachings of these references...that [Dillon's tetra-orthoesters] would operate to remove water from non-aqueous liquids by the same mechanism as the orthoesters of Sweeney." The Board also stated that the tri- and tetra-orthoester fuel compositions would have similar properties, based on "close structural and chemical similarity". The Commissioner argues on appeal that the claimed compositions and method "would have been prima facie obvious from combined teachings of the references." [The Board found that since Dillon failed to make a

showing that there was some unexpected advantage of her claimed tetra-orthoester fuel compositions as compared with tri-orthoester fuel compositions, the claims are unpatentable for obviousness.]

The issue before the court (en banc) was whether the Board erred in rejecting as obvious under 35 U.S.C. §103 claims to Dillon's new compositions and to the new method of reducing particulate emissions, when the additives in the new compositions are structurally similar to additives in known compositions, having a different use, but the new method of reducing particulate emissions is neither taught nor suggested by the prior art.

[The court agreed with the Board's decision and found that the PTO had established, through a combination of references, that there was a sufficiently close relationship between the tri-orthoesters and the tetra-orthoesters.]

The appellant cited *In re Wright*, 848 F.2d 1216, 1219, 6 USPQ2d 1959, 1961 (Fed. Cir. 1988) for the proposition that a prima facie case of obviousness requires that the prior art suggest the claimed composition's properties and the problem the applicant attempts to solve. The court reaffirmed a previous opinion that structural similarity between claimed and prior art subject matter, proved by combining references or otherwise, where the prior art gives reason or motivation to make the claimed compositions, creates a prima facie case of obviousness, the burden shifting to the applicant to rebut that prima facie case. [The court suggested the following remedies for the rebuttal: (1) comparative test data showing unexpected properties; (2) that there is no motivation to make what might otherwise appear to be obvious changes; and/or (3) any other argument or presentation of pertinent evidence. The court also stated that it is not necessary to have both a structural similarity between a claimed and prior art compound and that there be a suggestion in the prior art that the claimed compound will have the same or similar utility. Dillon did not present any showing of data to effect that her compositions had properties not possessed by the prior art. In addition, Dillon did not limit her claims to her new use but rather she recited and tried to claim compositions analogous to those in the Sweeney patents.]

[Dillon] attacks the Elliott patent as non-analogous art, being in the field of hydraulic fluids rather than fuel combustion. [The court] agreed with the PTO that the field of relevant prior art need not be drawn so narrowly. [They based their decision on the test of *In re Deminski*, 796 F.2d 436, 442, 230 U.S.P.Q. 313 (Fed. Cir. 1986) stating that one concerned with the field of fuel oil clearly is chargeable with knowledge of other references to tri-orthoesters, including for use as dewatering agents for fluids, albeit other fluids.]

The appellant urges that the Board erred in not considering the unexpected results of her invention and in not considering the claimed invention as a whole. The Board found [and the court agreed] that no showing was made of unexpected results for the claimed compositions compared with the compositions of Sweeney. [In fact], appellant's patent application included data showing that the prior art compositions containing tri-orthoesters had equivalent activity in reducing particulate emissions.

[The majority comments on the cases cited in the dissent saying that if] an examiner considers that he has found prior art close enough to the claimed invention to give one skilled in the relevant chemical art the motivation to make close relatives of the prior art compound(s), then there arises what has been called a presumption of obviousness or a prima facie case of obviousness. [They further make the comment that properties are relevant to the creation of a prima facie case in the sense of affecting the motivation of a researcher to make compounds closely related to or suggested by a prior art compound.]

[In the dissent by Newman, J., joined by Cowen, Senior Circuit Judge, and Mayer, Circuit Judge, the comment is made that] the ruling of this en banc court changes what must be proved in order to patent a new chemical compound or composition, and thus changes what is patentable. The majority holds that a prima facie case of obviousness is made whenever the structure of the applicant's new compound is "obvious" from that shown in the prior art, independent of whether the prior art suggests or makes obvious the applicant's newly discovered property and use. Thus, according to the majority, when the prior art chemical compound has no known use, the prior art provides no "reason or motivation" to make a structurally similar new compound or composition. The applicant is thus required to show "unexpected" properties and results, whether or not the prior art provides an expectation or suggestion of the properties and results disclosed in the patent application. And unless that applicant proves that the prior art structure does not actually possess the same unobvious property that the applicant discovered for the new structure, the court holds today that the new chemical compound is not patentable. (Explanation supplied.)

j. Making a Case for Novelty, Utility and Nonobviousness

The case for the novelty, utility and nonobviousness of a claimed invention is made while the patent is undergoing prosecution. Support of the invention and the willingness to protect it begins in the patent application stage, and the worth of building a thorough record and effectively prosecuting an application before the patent examiner should not be underestimated. The importance of effectively prosecuting an application becomes apparent as defects in prosecution taint the patent and tend to be magnified during licensing negotiations and in patent infringement litigation. In the next chapter, the patent prosecution process will be discussed.

Notes for Chapter II

1. 35 U.S.C. §102.
2. 35 U.S.C. §101.
3. 35 U.S.C. §103.
4. R. P. Merges, Patent Law and Policy, (Charlottesville, 1992), 4.
5. Peter D. Rosenberg, Patent Law Basics, (New York, 1992), 7-9.
6. Irving Kayton, Patent Property , (Washington, D.C., 1970), 269.
7. Irving Kayton, Patent Practice, (Washington, D.C., 1989), 5-1.
8. *In re A&P Tea Co. v. Supermarket Equipment Co.*, 340 U.S. 147, 87 U.S.P.Q.303 (1950).
9. *In re Miller*, 311 F.2d 955, 959, 136 U.S.P.Q. 205, 208 (C.C.P.A. 1963).
10. *In re Dillon*, 919 F.2d 688, 16 U.S.P.Q.2d 1897 (Fed. Cir. 1990), *cert. denied*, 111 S Ct. 1682 (1991).
11. *In re Papesch*, 315 F.2d 381, 391, 137 U.S.P.Q. 43, 51 (C.C.P.A. 1963).

CHAPTER III

Patent Prosecution

A. Overview of the Patent Prosecution Process

Patent Prosecution is the process of obtaining a patent from the United States Patent and Trademark Office (PTO). This process begins with the filing of a patent application in the PTO. The application is comprised of the following components: (1) a complete description of the invention; (2) a claim or claims which define the invention; (3) a drawing, if necessary, which explains the invention; (4) an oath or declaration stating that the applicant is the original inventor; and (5) a filing fee. Each of these elements must comply with various statutory requirements and with rules, which conform to the statute and have been established by the PTO.

After the application is filed, an examiner in the PTO studies the subject matter and conducts a search through all relevant prior U.S. and foreign patents and publications to determine if the invention has utility and is novel and nonobvious. Based on the examiner's findings, a decision is made by him concerning the patentability of the invention as claimed and whether the application meets various formal requirements. This decision is communicated in writing to the applicant or his practitioner. If the decision is adverse, the applicant may request reconsideration and can amend his application and/or claims or file remarks to overcome any rejections and/or objections. The application is then re-examined and reconsidered and the result is again communicated to the applicant. (All communications with the PTO are conducted in writing.)

If a showing is made that the invention is patentable, a patent is granted and the applicant is sent a Notice of Allowance. However, if a final decision by the examiner is adverse to the granting of a patent, based on the substance of the application, the applicant may appeal to the PTO Board of Patent Appeals and Interferences. This Board is a judicial-type body within the PTO itself. If the Board affirms the rection of the application, the applicant may either take an appeal to the U.S. Court of Appeals for the Federal Circuit or bring civil action against the Commissioner of Patents and Trademarks in the U.S. District Court for the District of Columbia and thence appeal to the Federal Circuit. This procedure is not followed when the examiner finally rejects an application based on form and procedure. Instead, the applicant must seek review by petitioning the Commissioner of Patents. The amount of time required to complete the prosecution process varies for each case depending on the circumstances surrounding it.

B. Detailed Analysis of Prosecution History

This section will focus on actual cases which have been filed in the PTO and have now issued as patents. A detailed analysis will be presented for inventions relating to the chemical arts. The statutory classes for the inventions discussed herein include composition of matter, process, and new use of a known composition. Because of the length of the applications, only the claims will be presented. The claims are considered to be the core of patent prosecution because it is the claim which defines the invention.

1. Composition of Matter

The invention described herein is for a composition of matter. More specifically, the invention is directed to di(hydroxyphenyl)-benzimidazole monomers which serve as precursors to polybenzimidazoles. The novelty of the invention is found in the structures of the monomers, which had not been previously prepared. The nonobviousness of the invention is found in the unexpected properties of the polymers which were prepared from these monomers. The polymers exhibited lower glass transition temperatures, improved solubility, and better compression moldability as compared to their commercial counterparts. These polymers are useful where a need exists for a material which would be subject to a harsh environment. Based on this analysis, claims were drafted for the invention reciting the structures of the benzimidazole monomers. (There are three ways in which to claim a composition of matter: (1) give the chemical name; (2) draw the structural formula; or (3) describe the process by which it is prepared.)

The application was filed as a divisional application in accordance with the rules of Title 37 of the Code of Federal Regulations section 1.60(b) (37 C.F.R. §1.60(b)). A divisional application results when there is more than one invention claimed in an original application and the examiner has issued a restriction requirement. When a restriction requirement occurs, the applicant must decide which invention to pursue first, reserving the right to file a separate (divisional) application(s) for the remaining invention(s) prior to the issuance of the first (parent) application. For the present case, the two inventions were directed to the benzimidazole monomers and the benzimidazole polymers. The claims to the benzimidazole polymers were prosecuted prior to and separate from the claims to the benzimidazole monomers. Section 1.60(b) allows the applicant to omit the signing of the oath and to file a copy of the parent application, cancelling the claims to the first invention (for this case the claims to the polymers were canceled). This is a short-cut technique to filing an application because there is no need to rewrite the application since the original application described and claimed multiple inventions. This explains why the specifications for many divisional patents may read the same yet the claims will be for different inventions. Typically, there is a statement at the beginning of the patent which identifies it as a divisional of either a copending application or an issued patent.

An amendment is a paper which is filed in the PTO by the applicant or his representative which makes some change to the application. Prior to the examination of the application, a preliminary amendment was filed in order to change the title of the specification and to correct errors which were found in the specification. The provision of 37 C.F.R. §1.115 allows for amendments prior to the first examination. However, when a decision is made to amend the specification, care must be taken so as not to add any new subject matter into the disclosure. Section 1.118 of 37 C.F.R. states:

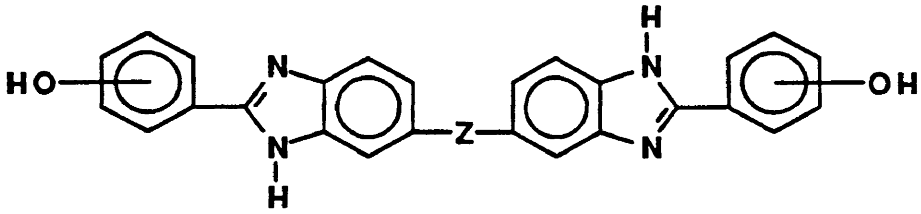
> (a) No amendment shall introduce new matter into the disclosure of an application after the filing date of the application (§1.53(b)). All amendments to the specification, including the claims, and the drawings filed after the filing date of the application must conform to at least one of them as it was at the time of the filing of the application. Matter not found in either, involving a departure from or an addition to the original disclosure, cannot be added to the application after its filing

> date even though supported by an oath or declaration in accordance with §1.63 or §1.67.
>
> (b) If it is determined that an amendment filed after the filing date of the application introduces new matter, claims containing new matter will be rejected and deletion of the new matter in the specification and drawings will be required even if the amendment is accompanied by an oath or declaration in accordance with §1.63 or §1.67.

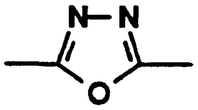
One of the changes made to the specification had to do with re-stating the field of the invention so that it related to di(hydroxyphenyl)benzimidazole monomers rather than polymers. Another change that was made was to delete the objects of the invention having to do with the making of polymers. The last change had to do with the addition of the phrase "20 ml DMAc (9.7% solids w/w) and stirring continued at 155-160°C. The viscous reaction mixture was diluted with". This phrase was accidentally omitted in the typing of the original application. It is not considered to be new matter because it was added to the specification to make the sentence make sense. The claims for the invention are presented below.

What is claimed is:

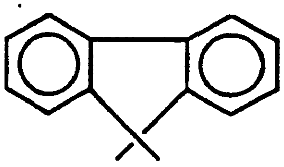
1. A di(hydroxyphenyl)benzimidazole monomer having the following general structure:



where z is selected from the group consisting of: nil, $-CH_2-$, -O-, -S-, -CO-, $-SO_2-$,



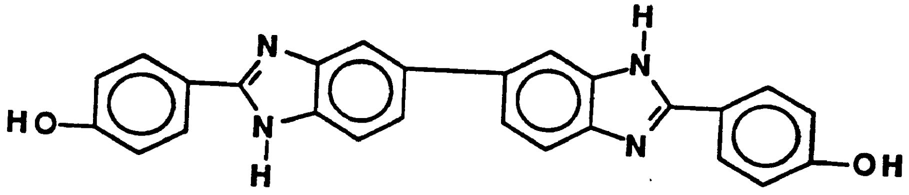
and



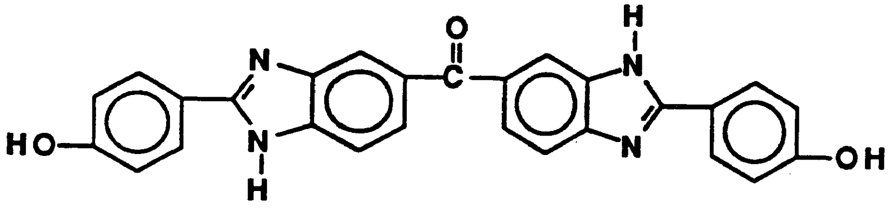
; and

the catenation of the hydroxy groups is selected from the group consisting of: meta-meta, para-para, and para-meta.

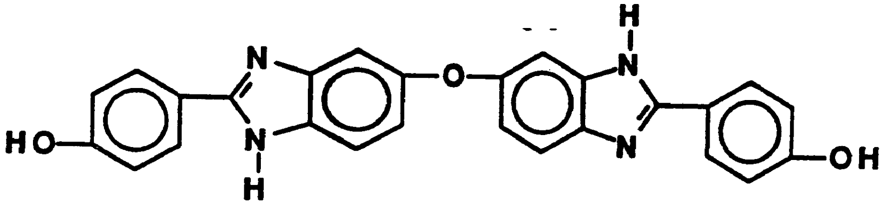
2. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:



3. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:



4. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:



In the examiner's first and only office action, claim 1 was rejected under 35 U.S.C. §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the applicant regards as the invention. The term "general" was considered by the examiner as indefinite since it suggests that the compounds have other structures not contemplated by the applicants. The term "nil" was also considered by the examiner to be be unclear to its meaning. The examiner also rejected claim 2 and objected to claims 3 and 4 under 35 U.S.C. §112 because they are dependent on claim 1. (A dependent claim is that which refers to a preceding claim, where an independent claim does not refer to a previous claim.) Claim 1 was amended to delete the words "general" and "nil" so as to overcome these rejections and objections. The phrase "a direct bond" was substituted for the word "nil". In order to make these changes, there must be basis in the original specification so as not to constitute new matter within the prohibition of 37 C.F.R. §1.118. The basis for the changing of the word "nil" to "a direct bond" is found in original claim 2, where it is shown that z is a direct bond. (The originally filed claims are considered to be part of the specification.) In reference to the deletion of the word "general", this change would not effect the meaning of the claim so as to constitute new matter. It is only for clarification.

The examiner also rejected claim 1 under 35 U.S.C. §103 as being unpatentable over the combined teachings of Sues et al. and Kalle & Co. Akt.-Ges. The examiner asserted that Sues et al. and Kalle & Co. Akt.-Ges teach structurally similar compounds that differ only in having a methyl attached to the nitrogen of the benzimidazole ring. Thus, the applicants' compounds were deemed to be obvious optional variants of the compounds of Sues et al. and Kalle & Co. Akt.-Ges. The examiner asserted that in view of the close structural similarity, the variation of hydrogen and methyl is an obvious modification. The examiner further contended that the exact utility here is not required in the references when this type of close structural similarity is obvious to one of ordinary skill in the art. This argument refers to the ruling of *In re Dillon*, discussed supra.

In order to overcome this rejection, arguments were made showing the unexpected polymer properties of low glass transition temperature (Tg) and increased solubility. The specific argument was made that the monomers based on the bis(hydroxy)benzimidazole structure have a N-H bond. The N-H bond causes hydrogen bonding to occur in both the monomers and the polymers made therefrom. In addition to the N-H bond, these monomers are bisphenol benzimidazoles which lead to polymers containing additional ether linkages. These additional ether linkages give rise to the unexpected propertites of low Tg and increased solubility as discussed in the specification.

Sues et al. and Kalle & Co. Akt.-Ges disclose bis(hydroxy)N-alkyl benzimidazoles. Since these monomers are substituted, hydrogen bonding does not occur. The presence of hydrogen bonding gives rise to high-temperature structural properties which are not present in the substituted monomers. (An article entitled "Polyimidazoles" was submitted as evidence to support the aforementioned statement.) The conclusion was made that the variation of hydrogen and methyl is not an obvious modification as the final properties obtained for the polymers prepared from these monomers are not the same.

The examiner allowed the case based on this argument. The patent, U.S. 5,245,044, issued on September 14, 1993. A copy of this patent is attached in the Appendix.

2. <u>New Use of a Known Composition</u>

We turn now to another type of composition of matter invention. The application filed for this invention demonstrates a way to obtain patent coverage for a known composition of matter. It is termed a "use patent" or a new use of a known composition and is expressed in terms of a process. This type of coverage is provided for in 35 U.S.C. §100(b) which states:

> (b) The term "process" means process, art or method, and includes a new use of a known process, machine, manufacture, composition of matter, or material.

The invention, as filed, is for a process for preparing an assembly of an article and a soluble polyimide which resists dimensional change, delamination, and debonding when exposed to changes in temperature. This particular invention is of interest. When the inventors had originally filed their disclosure, they wished to claim a metal ion-containing polyimide having a low coefficient of thermal expansion (CTE) as a composition of matter. However, this was not possible because the inventors had disclosed the same composition in a publication two years prior to discovering that these polyimides had low CTEs. This presented a statutory bar under 35 U.S.C. §102(b), which was discussed supra.

The inventors were concerned with obtaining coverage for these polyimides because they were particularly useful for space applications. Since, 35 U.S.C. §100(b) provides for the patenting of a new use of a known composition, that was the approach which was taken in seeking coverage for the previously disclosed metal ion-containing polyimide. Thus, the process for preparing an assembly of an article and a low CTE polyimide was claimed. The novelty of the invention lies in the process itself and the nonobviousness of the invention is found in the fact that the assembly resists dimensional change, delamination, and debonding when exposed to temperature changes.

Once the decision was made to seek coverage on the use of the material, there was one more obstacle to overcome. The inventors had not actually prepared the assemblies which they wished to claim as their inventions. Thus, there was a problem with meeting the best mode requirement of the specification. This requirement is found in 35 U.S.C. §112, first paragraph. Usually, this requirement does not present a problem until an infringement or declaratory judgement action arises. In *Dana Corp. v. IPC Limited Partnership*, 860 F.2d 415, 8 U.S.P.Q.2d 1692 (Fed. Cir. 1988), the Federal Circuit stated: "If, in fact, the best mode contemplated by the inventor has not been disclosed for a claimed invention, then the claims for that invention in any patent issuing from that application will be invalid." The patent office allows for the use of "prophetic" or "paper" examples in order to fulfill the best mode requirement of 35 U.S.C. §112, first paragraph. Prophetic examples are simply statements by the applicant as to how a working example should be carried out, even though he has not actually done so. As a rule they are written in the present tense as opposed to the past tense, which is typically used. Thus, prophetic examples were used in the instant application to meet the best mode requirement. The claims for the invention are presented below.

What is claimed is:

1. A process for preparing an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes, the process comprising:

   a. providing an article;

   b. preparing a soluble polyimide resin solution with a reduced coefficient of thermal expansion by dissolving a soluble polyimide in solvent to which is added a metal ion-containing additive selected from the group consisting of: $Ho(OOCCH_3)_3$, $Er(NPPA)_3$, $TmCl_3$, $Er(C_5H_7O_2)_3$; and

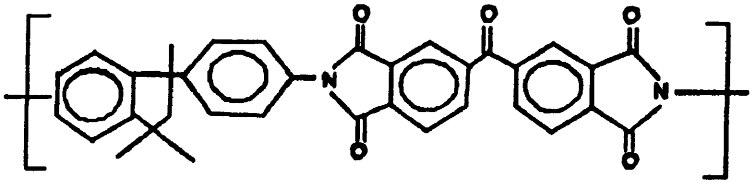
   c. heating the soluble polyimide resin solution and combining it with the article to form the assembly.

2. The process of claim 1, wherein said article is selected from the group consisting of: solar concentrators, antennae, solar cell arrays, second surface mirrors, precision solar reflectors, and electronic circuit boards.

3. The process of claim 2, wherein said article is a precision solar reflector.

4. The process of claim 1, wherein the concentration of said soluble polyimide resin solution is about 10-15 weight percent.

5. The process of claim 1, wherein said polyimide has the repeat unit:



6. The process of claim 1, wherein said solvent is selected from the group consisting of: N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-pyrrolidone, dimethylsulfoxide, and bis(2-methoxyethyl)ether.

7. The process of claim 6, wherein said solvent is N,N-dimethylacetamide.

8. The process of claim 1, wherein the concentration of said metal ion-containing additive is 4-30 percent.

9. The process of claim 1, wherein said metal ion-containing additive is $Er(C_5H_7O_2)_3$.

10. The process of claim 1, wherein said soluble polyimide resin solution is used to coat the article prior to heating for solvent removal.

11. The process of claim 1, wherein said soluble polyimide is heated to form a substrate and the article is bonded to the resulting imide substrate.

12. The process of claim 11, wherein the article is bonded to the imide substrate by embedding the article in the solution prior to heating.

13. The process of claim 11, wherein the article is bonded to the imide substrate with an adhesive.

14. The process of claim 11, wherein the article is bonded to the imide substrate by using a surface treatment.

15. The process of claim 14, wherein the article is selected from the group consisting of: highly reflecting silver, aluminum, and chromium and said surface treatment is vapor deposition.

16. The process of claim 14, wherein the article is selected from the group consisting of: highly reflecting silver, aluminum, and chromium and said surface treatment is sputtering.

17. The process of claim 1, wherein said soluble polyimide is made from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(aminophenoxy)benzene.

In the Office Action, the examiner objected to the specification under 35 U.S.C. §112, first paragraph, as failing to adequately teach how to make and/or use the invention, i.e. failing to provide an enabling disclosure. In particular, the examiner questioned how the polyimide substrate was formed. The descriptive phrase, "by casting the soluble polyimide solution into a mold and heating to about 100°-300°C" was added to the specification. The addition of this phrase to the teachings was permitted because it was disclosed in the working examples. Thus no new matter was added under 37 C.F.R. §1.118.

The examiner rejected claims 1-10 and 17 under 35 U.S.C. §112, first paragraph. More specifically, the examiner asked how the soluble polyimide resin solution was prepared. Amendments were made to the claims which showed that a solution of a soluble polyimide resin was prepared by dissolving the polyimide in a particular solvent.

The examiner rejected claims 1, 4, 8, 10 and 17 under 35 U.S.C. §112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which the applicant regards as the invention. The amendments which were made to the claims to overcome the first paragraph rejection provided the proper clarification.

Claims 1-10 and 17 were rejected under 35 U.S.C. §103 as being unpatentable over Okinoshima et al. (U.S. 5,041,513) in view of Kimura (U.S. 4,574,056). The reference to Okinoshima et al. was argued first. Okinoshima et al. teach the preparation of a polyimide resin soluble in an organic solvent. The resin solution is applied to the substrate and heated until the solvents evaporate off, obtaining resin films. Okinoshima et al. also disclose the solvent can be N-methyl-2-pyrrolidone, N,N'-dimethylformamide, and N,N'-dimethyl-acetamide, while the diamine can be 1,3-bis(4-aminophenoxy)benzene.

The argument was made that by the present invention, an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes is prepared by: (a) providing an article; (b) preparing a solution of a soluble polyimide resin with a reduced coefficient of thermal expansion by dissolving a soluble polyimide resin in a solvent selected from the group consisting of: DMAc, chloroform, methyl ethyl ketone, and isobutyl ketone to which is added a particular metal ion-containing additive; and (c) heating the solution of a soluble polyimide resin and combining it with the article to form the assembly (claim 1). Okinoshima et al. disclose polyimide resin compositions which are readily applicable to substrates, typically providing insulating protective coatings on electronic parts. The polyimide resin solution of Okinoshima et al. would be an example of the soluble polyimide resin to which a metal ion-containing additive could be added according to the present invention to yield a solution with a reduced coefficient of thermal expansion.

Furthermore, the argument was made that there is no teaching or suggestion of the process for preparing an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes. Nor does the reference teach or suggest the addition of a metal ion-containing additive (claims 1, 8, and 9). Rather, Okinoshima et al. disclose only the preparation of a polyimide resin solution which might be useful in forming the assembly of the present invention.

Next, the reference to Kimura was discussed. Kimura (U.S. 4,574,056) discloses a die-bonding electroconductive paste containing at least one element having the same valence as the valence of a semiconductor element to be die-bonded. There is no mention or suggestion of the preparation of an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes. The Examiner asserted that Kimura teaches the use of lanthanides to increase the chemical affinity between metals and polymers. The Examiner further stated that Kimura also teaches the use of a polyimide solution. However, there is no mention that the polyimide solution has a reduced coefficient of thermal expansion.

The Examiner argued that it is well known that the use of lanthanides or its compounds are used to increase the adhesion between metals and polymers as evidenced by Kimura. However, the counter-argument was made that not all lanthanides worked for the present invention as was shown by the Markush group of claim 1. This helped to establish the non-obviousness of the invention. The Examiner argued further that it is well known in the coating art to use a metal-organic material to increase the adhesion between metals and polymers, and to incorporate a lanthanide compound such as $Er(C_5H_7O_2)_3$ in Okinoshima et al. would have been obvious with the expectation of increasing adhesion. Applicants disagreed with this reasoning in that there was no basis in the specification of either Okinoshima et al. or Kimura to combine the two references. The polyimide resin solution of Okinoshima et al. is applicable as protective coatings for electronic parts where the invention of Kimura is that of a die-bonding electroconductive paste which permits ohmic contact with a semiconductor element.

Okinoshima et al. teach many applications for the polyimide resin solution including printed circuit boards. It was the Examiner's position that a solar reflector falls into this category of applications and, hence meets the limitation of claim 3. The Examiner further suggested that to substitute one article for another is conventional and would have been obvious depending on the final use of the product. Okinoshima et al. do not disclose the process for preparing and assembly of a solar reflector and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes. Furthermore, nowhere in their specification do Okinoshima et al. mention subjecting their finished product to temperature changes.

Lastly, the Examiner took the position that the applicant's requirement that the resin solution is about 10 - 15 weight percent is met by Okinoshima et al. and regardless, to vary the weight percent of the resin solution is conventional and well known in the coating art and hence would have been obvious to vary with the expectation of obtaining optimum deposition conditions. It is conceded that Okinoshima et al. does mention the same percentage requirement of the resin solution, however, they fail to mention that combined with the polyimide resin solution is a metal ion-containing additive to form a soluble polyimide resin solution with a reduced coefficient of thermal expansion.

Neither of the references teach or suggest the preparation of a soluble polyimide resin solution with a reduced coefficient of thermal expansion by dissolving a soluble polyimide in solvent to which is added a particular metal ion-containing additive. Nor do they disclose the process for preparing an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes (claim 1).

The final statement was made that the combination of art cited did not result in the present invention as claimed. Moreover, as the cited art does not contain some teaching, suggestion, or incentive to combine the individually disclosed features in the manner recited in the instant claims, the claims are not obvious under 35 U.S.C. §103 in view of the cited art.

The examiner withdrew the rejections and objections based on these arguments. The patent issued on September 28, 1993, as U.S. 5,248,519. A copy of the patent is attached in the Appendix.

3. Chemical Process

We will now move from patenting a known composition of matter as a process to patenting new processes. The invention is an aqueous slurry technique for preparing polymeric matrix composites. This process is particularly useful where it is desired to prepare uniform and processable consolidated composite laminates from polymers which are difficult to process. The process or technique, itself, is novel in that it has never been done before. The key to the process lies in the use of a poly(amic acid) salt which acts as a surfactant for polymeric powders in an aqueous system. The nonobviousness of the invention is based on the unexpected finding that the composite laminates prepared using this technique exhibited high fracture toughness and excellent consolidation. Based on this analysis, the following claims were filed:

What is claimed is:

1. An aqueous process for preparing a consolidated composite laminate comprising:

   (a) preparing an aqueous poly(amic acid) surfactant solution comprised of a poly(amic acid) powder and an aqueous ammonia solution;

   (b) forming an aqueous slurry comprised of the poly(amic acid) surfactant solution and polymeric powder;

   (c) depositing the aqueous slurry on carbon fiber to form a prepreg;

   (d) drying the prepreg;

   (e) stacking the prepreg to form a composite laminate; and

   (f) consolidating the composite laminate at pressures from about 300 - 1000 psi and heating at a temperature to imidize the poly(amic acid) and to impart melt flow in the polymeric powder.

2. The process of claim 1, wherein said poly(amic acid) surfactant solution is about 3% solids poly(amic acid).

3. The process of claim 1, wherein said aqueous slurry is about 5-20% solids polymeric powder.

4. The process of claim 1, wherein said polymeric powder is selected from the group consisting of: polyimide, poly(arylene-ether), polysulfone, polybenzimidazole, and liquid-crystalline polymers.

5. The process of claim 4, wherein said polymeric powder is a polyimide.

6. The process of claim 1, wherein said aqueous slurry is deposited on the carbon fiber by dipping.

7. The process of claim 1, wherein said prepreg is dried at room temperature.

8. The process of claim 1, wherein said prepreg is dried in a forced-air oven.

9. The process of claim 1, wherein said pressure is 1000 psi.

10. The process of claim 1, wherein said poly(amic acid) surfactant solution imidizes and forms a blend with the polymeric powder.

11. The process of claim 1, wherein said poly(amic acid) solution binds the polymeric powder to the carbon fiber.

The rejections made by the examiner for this application provide a classic example of how art is combined in an attempt to arrive at the instant invention. This is more simply referred to as: A + B + C + ... = the invention. Thus, in order to overcome this type of rejection, one need only eliminate one of the references. If this is not possible, as was the case here, one must show that the combination of references is not tantamount to the invention as claimed, taking each reference for what it, as a whole, reasonably teaches. The examiner rejected claims 1-11 under 35 U.S.C. §103 as being unpatentable over Pike (U.S. 4,601,945) in view of Pike (U.S. 4,480,088) and Kanda et al. (U.S. 4,442,248). Pike ('945) discloses the formation of fiber reinforced polyimide matrix composite articles...via a process in which graphite (i.e. carbon) fiber...is coated/impregnated...with an aqueous solution of a polyimide prepolymer matrix material wherein said aqueous solution contains sufficient surfactant to cause the surface tension of the solution to be about 35 dynes/cm or lower...dried and formed into prepregs; a plurality of these prepregs are then stacked and subjected to the action of heat and pressure to imidize the polyamic acid and form the composite article...Any water soluble polyamic acid may be employed in the aqueous solution,...which solution is applied to the fiber in any conventional manner e.g. dipping etc...

The argument was made that there is no mention of an aqueous slurry in Pike ('945). Instead, Pike emphasizes the importance of lowering the surface tension to obtain an improved composite. Nor does Pike teach or suggest that the poly(amic acid) solution is used as a surfactant. Rather, Pike discloses that a nonionic surfactant or wetting agent is required to lower the surface tension of the aqueous solution of the polyamic acid. Pike fails to teach or suggest the formation of a surfactant by the combination of a poly(amic acid) powder and an aqueous ammonia solution.

Pike ('088), which was cited by the applicants in their specification, discloses that it is known to form polyimides (used as coating materials)...via a process in which a polyimide resin is precipitated from its organic solvent as a polyamic acid through the addition of water, washing the precipitate free of the organic solvent, drying the resin and redissolving the resin in dilute ammonium hydroxide to form an aqueous solution of the polyimide resin,...which solution is applied to the substrate to be coated and heated thereon to form the polyimide...Any imidizable polyamic acid may be employed.

The argument was made that Pike ('088) does not disclose the formation of an aqueous slurry comprised of a poly(amic acid) surfactant solution and a polymeric powder. Nor does he teach or suggest the preparation of a consolidated composite laminate by depositing the aqueous slurry on carbon fiber to form a prepreg and stacking the prepreg to form a composite laminate which is consolidated under pressure and temperature (claim 1). Rather, he discloses a process for making water soluble polyimide resin systems (to which no additional polymeric powder is added) which are used for safer applications of polyimide coatings to substrates.

Kanda et al. ('248) disclose that it is known to utilize a water soluble or water dispersible resin which has been formed by reaction between carboxyl bearing and amino bearing monomeric components/reactants...and subsequently treated with a basic substance (e.g. ammonia) or with an acid to effect the neutralization...in conjunction/combination with a finely divided/powdered water insoluble thermoplastic resin (which may be an engineering resin/polymer e.g. polycarbonate) in the aqueous resin varnish...which finds utility as a coating material,...the use of the water soluble/dispersible resin insuring that the content of the water insoluble resin may be increased without a resultant increase in the viscosity of the aqueous composition.

The argument was made that Kanda et al. do not teach or suggest an aqueous process for preparing a consolidated composite laminate comprising the preparation of a poly(amic acid) solution which acts as a surfactant. Nor do they disclose the formation of an aqueous slurry comprised of the poly(amic acid) surfactant solution and a polymeric powder which is deposited onto carbon fiber to form a prepreg which is dried, stacked, and consolidated to give a composite laminate.

The examiner asserted that it would have been obvious to one of ordinary skill in the art to employ the water soluble polyamic acid salt disclosed in Pike ('088) as the water soluble polyamic acid used in the Pike('945) process in conjunction with the finely divided/powdered thermoplastic resin documented in Kanda et al. for use with ammonia treated resins derived from carboxyl and amino bearing reactants, in the formation of fiber reinforced composites of the type shown in Pike ('945); mere substitution and use, respectively, of known conventional materials employed in the formulation of aqueous coating compositions involved.

The argument was made that the combination of art cited did not teach the formation of a surfactant by the combination of a poly(amic acid) powder and an aqueous ammonia solution, where the surfactant is further utilized in the formation of an aqueous slurry comprised of the poly(amic acid) surfactant solution and a polymeric powder. The aqueous slurry is deposited on carbon fiber forming a prepreg which is stacked and consolidated to form the composite laminate. In particular, the combination of art does not describe the utilization of the combination of the poly(amic acid) powder and aqueous ammonia solution as a surfactant for other polymeric powders in the formation of an aqueous slurry useful for the formation of consolidated composite laminates, but rather provides an aqueous system with a low surface tension.

The examiner rejected claims 4 and 5 under 35 U.S.C. §103 as being unpatentable over Pike ('945) in view of Pike ('088), Kanda et al. ('248) and Von Bonin et al. (U.S. 4,169,866). The examiner asserted that Von Bonin et al. disclose that it is known to utilize a thermoplastic polycarbodiimide resin...in combination with a thermoplastic (e.g. engineering) resin (to include polycarbonate, polyether and polysulfone)...in the formulation of a multi-component thermoplastic composition utilized in the formation of e.g. fiber reinforced plastic composites such that it would have been obvious to one of ordinary skill in the art to employ any of the thermoplastic engineering resings documented in Von Bonin et al. as the thermoplastic (e.g. engineering) resin employed in the composition of Kanda et al. (which reference was used to modify the Pike ('945) reference as was set forth previously). The counter-argument was made that Von Bonin et al. teaches thermoplastic multicomponent molding materials, so-called polymer systems which contain at least one polymeric polycarbodiimide. More specifically, the invention relates to thermoplastically processible polymer systems of vinyl polymers and polycarbodiimides, which are not the same as polyimides. Polycarbodiimides can be produced by reacting a compound containing at least two isocyanate-reactive hydrogen atoms with a stoichiometric excess of diisocyanates or polyisocyanates to form an isocyanate prepolymer to which a catalyst is added, converting the prepolymer to the corresponding polycarbodiimide. A polyimide is prepared by reacting an anhydride of a tetracarboxylic acid with an amine in an organic solvent forming a polyamic acid which is heated to a high temperature to form the polyimide. Accordingly, there is no basis in any of the cited references to combine Von Bonin with Pike and Kanda et al.

Lastly, it was pointed out to the examiner that the combination of art cited does not result in the present invention as claimed. In view of the above arguments, the examiner withdrew his rejections and the patent issued on October 12, 1993 as U.S. 5,252,168. A copy of the patent is found in the Appendix.

C. Patentability Summaries for Inventions which have Issued as Patents

In this section nine inventions, relating to the chemical arts and all of which have now issued as patents, are presented. A brief summary of how each one of these inventions meets the requirements for patentability is given.

1. U.S. 5,213,843: Vacuum Powder Injector and Method of Impregnating Fiber with Powder

This invention is classified in the statutory classes of method and apparatus (or machine). The utility requirement for this invention is met in that it may be used to prepare composite prepregs for the aerospace and aircraft industries. The novelty of the invention lies in the structure of the apparatus which uses an impregnation chamber which allows for the expansion of air, whereby stranded material expands and becomes impregnated with powder. The nonobviousness requirement is met by the fact that the impregnation chamber allows the fiber and the powder to travel parallel to each other. This is in contrast to the method and apparatus of the prior art whereby the powder is applied perpendicularly to the fiber.

2. U.S. 5,200,497: Polyimide from Bis(N-Isoprenyl)s of Aryl Diamides

This invention is classified as both a composition of matter and a process invention. The composition of matter is a new polyimide which is prepared by the process where an excess of an acid chloride is reacted with 1,4-N,N'-diisoprenyl-2,3,5,6-tetramethyl benzene to form a bis(amidediene). This novel bis(amidediene) undergoes a Diels-Alder reaction with a bismaleimide, without the evolution of gasesous by-products, to form the novel aromatic polyimide product. These polymers are useful for space applications where it is important that they maintain their integrity and toughness during long exposure times at elevated temperatures. The nonobviousness of the composition of matter invention lies in the unexpected properties which characterize this polymer[1], where the nonobviousness requirement of the process invention is met by the use of an acid chloride to form a bis(amidediene).

3. U.S. 5,182,356: Poly(1,2,4-Triazole) via Aromatic Nucleophilic Displacement

This patent covers two statutory classes: composition of matter and process. The novelty of the invention lies in the chemical structures of these polymers and the process to prepare them (i.e. aromatic nucleophilic displacement). These polymers are useful as composite matrix resins for aircraft and as dielectric interlayers for electronic devices. The nonobviousness of the composition of matter invention is found in the unexpected polymer properties, where the nonobvious requirement for the process invention is met by the preparation of these polymers via aromatic nucleophilic displacement.

4. U.S. 5,245,043: Di(Hydroxyphenyl)-1,2,4-Triazole Monomers

This patent is a divisional of U.S. 5,182,356. It is classified as a composition of matter. In particular a novel monomer which may be used to prepare poly(1,2,4-triazoles). These polymers are useful as composite matrix resins for aircraft and as dielectric interlayers for electronic devices. The surprising properties of the polymers prepared from these monomers is what establishes the nonobviousness of the invention.

5. U.S. 5,212,276: Polyimides with Improved Compression Moldability

The claims of this patent are for an invention which is classified as both a composition of matter and an article of manufacture. These polyimides are useful for preparing composites, molding materials, and adhesives (all of which are claimed). The novelty of the invention lies in the polyimide structure which is a polyimide endcapped with a monofunctional amine. The nonobviousness of the invention is established by the unexpected properties of these polyimides which include processability at lower temperatures and pressures than their corresponding non-endcapped polymers.

6. U.S. 5,189,129: High Temperature Polymer from Maleimide-Acetylene Terminated Monomers

This patent covers new compositions of matter which are useful for high temperature applications. In particular, these maleimide-acetylene terminated oligomeric materials can be polymerized with themselves, bismaleimide monomers, bis-acetylene monomers or mixtures thereof. The novelty requirement of the invention is met by the structure of the maleimide-acetylene terminated materials. The nonobviousness of the invention is that these oligomers have surprisingly lower melting temperatures and a broader processing window than those of the prior art.

7. U.S. 5,212,283: Polyimides Containing the Cyclobutene-3,4-Dione Moiety

This patent claims compositions of matter and articles of manufacture. The novel composition of matter is a polyimide which contains the cyclobutene-3,4-dione moiety. These polyimides are useful for flims, adhesives and coating whcih are exposed to a highly oxidative environment. The nonobviousness requirement is met by the unexpected properties exhibited by these polymers which include high glass transition temperatures, excellent adhesion to glass and increased flexibility with increasing cure temperatures.

8. U.S. 5,220,070: 1,3-Diamino-5-Pentafluorosulfanylbenzene

The invention is classified as a composition of matter which is useful for preparing semi-permeable membranes, wire coatings and films. The novelty requirement of the invention is met by the structure of the diamine, itself. The nonobvious feature of the invention is the process used to prepare the diamine which involves the use of a palladium catalyst to reduce the dinitro group to the diamine.

9. U.S. 5,189,127: Crosslinked Polyimides Prepared from N-(3-Ethynylphenyl)-Maleimide

This patent covers a new composition of matter which is used to make adhesives, coatings and films. The novelty requirement of the invention is met by the structure of the monomer which contains carbon-carbon double and/or triple bonds. The nonobviousness of the invention is found in the surprisingly highly reactive nature of the monomer as a result of its two types of unsaturation which, when polymerized, forms polymers which do not exhibit glass transition temperatures below 500°C.

D. Patentability Summaries for Allowed Cases

The following patentability summaries are for four cases which have undergone prosecution and have been allowed. The patents have not yet issued because either the issue fee has not yet been paid or they are in the process of being type-set at the PTO.

1. Polybenzimidazoles Via Aromatic Nucleophilic Displacement

This case was the parent case of "Di(hydroxyphenyl)-Benzimidazole Monomers", discussed supra. It is interesting to note that the patent for this case will issue after the patent for the daughter case has issued. The claimed invention relates to compositions of matter, a process for preparing the compositions, and articles prepared from the compositions The polymers of this invention may be used to prepare films. The novel feature of the invention is the structure of the polymers and the process in which they are prepared (aromatic nucleophilic displacement). The nonobviousness requirement is met by the showing of the unexpected property of increased solubility of these poly(benzimidazoles) over those of the prior art.

2. Tough, Processable Semi-Interpenetrating Polymer Networks from Monomer Reactants

This invention covers a process, a composition of matter, and articles of manufacture. By the present invention, tough processable polyimide composites were prepared by forming a semi-IPN from two monomer precursor solutions. The novelty of this invention is found in the formation of a semi-IPN comprised of two monomeric precursor solutions, NR-150B2 and Thermid®AL-600. The presence of the NR-150B2 solution broadens the processing window in the first stage of the reaction and increases the flow and rate of crosslinking in stage two. This provides a high temperature system having improved processability and outstanding thermal mechanical performance, something which was never previously achieved with these materials.

3. Tough, Processable Simultaneous Semi-Interpenetrating Polyimides

This case is related to the case, "Tough, Processable Semi-Interpenetrating Networks from Monomer Reactants", described above. The claims cover a process and articles of manufacture. The utility of this invention is the same as that for the invention above. The novelty of the invention lies in the formation of a semi-IPN comprised of the monomeric precursor solution, NR-150B2, and an acetylene-terminated oligomer selected from the Thermid® series. As with the invention above, the nonobviousness requirement is fulfilled by the system having improved processability and outstanding thermal mechanical performance, something which was never achieved with these materials before.

An interesting note about these two cases is that during their prosecution, the examiner provisionally rejected claims in both applications under the judicially created doctrine of obviousness-type double patenting. "This doctrine is based on public policy rather than statute and is primarily intended to prevent prolongation of the patent term by prohibiting claims in a second patent not patentably distinguishing from claims in a first patent. " (MPEP 804) Since these applications were co-pending and no patent had yet issued, the rejection was "provisional"[2].

This rejection was overcome by the argument that although it may appear that the products of the two applications are the same, they are in fact very different. In the present invention, an uncrosslinked preimidized oligomer is crosslinked in the presence of the monomer precursor solution, NR-150B2. The constituent thermosetting and thermoplastic polymers are formed independently without any chemical interference between the precursors of the two polymer components. In the related invention, described above, an inter-reaction between the monomers of the thermoset and the thermoplastic monomers takes place which results in the formation of many products and a semi-IPN which is significantly different in chemical structure and properties from those prepared by the method of the instant application.

4. Low Pressure Process for Continuous Fiber Reinforced Polyamic Acid Resin Matrix Composite Laminates

This invention is classified as a process which is used for compression molding of a composite laminate. The novelty of the invention lies in the use of molding stops which allow for the volatile by-products of the imidization reaction to escape. The nonobviousness requirement of the invention is met by the surprising showing that the consolidated composite laminate is void free.

It is interesting to note that this case received a first action allowance. There were no rejections based on the technical requirements of patentability.

E. Summary of Pending Cases

The following cases are currently pending in the patent office. They are in various stages of the prosecution process. A brief summary of how each case meets the requirements of patentability and the stage of prosecution is presented.

1. Vacuum Powder Injector and Method of Impregnating Fiber with Powder

This case was filed as a continuation of U.S. 5,213,843, discussed above. The claims in this case are directed to the method of making impregnated stranded material. These claims were not allowed in the parent case, so they were divided out in order to allow the parent case to issue. It is hoped that by filing and prosecuting this application, broader coverage may be obtained for the method of this invention. The invention is useful for making impregnated stranded material which may be later used to make composites. The novelty of the invention is found in the method itself. The nonobviousness requirement of the invention is met by showing that the powder and the stranded material are fed into a chamber whereby the powder and the fiber are expanded with air to allow for impregnation. Prior art methods involve "sprinkling" the fiber with powder as the fiber passes under a feed pipe. The claims in this case currently stand finally rejected under 35 U.S.C. §102(e) and 35 U.S.C. §103. A notice of Appeal has been filed in accordance with 35 U.S.C. §134, which states: "An applicant for a patent, any of whose claims has been twice rejected, may appeal from the decision of the primary examiner to the Board of Patent Appeals and Interferences, having once paid the fee for such appeal". An appeal allows for review of the examiners' rejections of claims based on statutory grounds (rejections on the merits).

2. Compounds Containing Meta-Biphenylenedioxy Moieties and Polymers Therefrom

The claims in this application are directed to compositions of matter and articles of manufacture. More specifically, a novel diamine and a novel dianhydride containing meta-biphenylenedioxy moieties and polymers prepared therefrom are claimed. These polymers are used to prepare films, coatings and selective membranes. The nonobvious feature of the invention is found in the fact that the glass transition temperatures of the polymers prepared from these monomers were 25 - 118°C lower than polymers prepared with monomers having para-biphenylenedioxy moieties.

The examiner placed a restriction requirement on the application. A restriction requirement is defined by the Manual of Patent Examining Procedure 802.02 as:

> Restriction, a generic term, includes that practice of requiring an election between distinct inventions, for example, election between combination and subcombination

> inventions, and the practice relating to an election between independent inventions, for example, and election of species.

Basis for this requirement is found in 37 C.F.R. §1.142. For this case, it was found that the claims in the application were directed to four distinct inventions: (1) a diamine or dianhydride; (2) a polyimide and article; (3) a polyamide; and (4) an epoxy. In order to proceed with the prosecution, a single group of claims must be elected. The claims directed to the diamine or dianhydride were elected for prosecution. There has been no action on the merits of the invention.

3. A Process for Preparing an Assembly of an Aritcle and a Polyimide which Resists Dimensional Change, Delamination, and Debonding when Exposed to Changes in Temperature

This case is related to the new use of a known composition case discussed in detail supra. The difference between the claims of this invention and those of the issued patent lies in the use of a polyamic acid solution instead of a soluble polyimide. The utility of the invention is found in the preparation of articles which resist dimensional change, delamination and debonding when exposed to changes in temperature. The novelty of the invention lies in the process (a polyamic acid solution is used instead of a soluble polyimide) and the nonobviousness of the invention is found in the fact that the assembly unexpectedly resists dimensional change, delamination and debonding when exposed to changes in temperature. This case has undergone much prosecution. The claims have been rejected under 35 U.S.C. §103 for obviousness based on the combination of four different patents. Despite amending the claims and arguing the references, the originally filed application was finally rejected. Upon final rejection, a Notice of Appeal was filed and a Continuation of the case was filed. The examiner rejected the claims based on the rejections of the parent case. The claims have been amended for a third time and new arguements presented.

4. Tough, Processable Simultaneous Semi-Interpenetrating Polyimides

This case is a continuation of the allowed case mentioned above. Claims in this case are directed to the composition of matter prepared by reacting an uncrosslinked, acetylene-terminated thermosetting polyimide prepolymer with a mixture of monomer precursors of a linear thermoplastic polyimide. Articles prepared from this composition are also claimed. These articles include: adhesives, composites, and molding compounds. The novelty of the invention is found in the structure of the polymer. The nonobviousness requirement is met by the properties of the polymers where there is unexpectedly improved flexural strength and interlaminar shear strength over those polymers of the prior art.

A continuation of the allowed case was filed for the claims which were not allowed in the parent case. The examiner had rejected the composition claims based under 35 U.S.C. §102(e) or alternatively under 35 U.S.C. §103 as obvious in view of the prior art. An affidavit was filed by the applicant showing that the properties of the polymers of the present invention are unexpectedly improved over those of the prior art.

5. Non-Rectangular Towpreg Architectures

The claims of this application are directed to articles of manufacture, more specifically to a shaped towpreg ribbon and a composite prepared therefrom. The novelty of the invention resides in the non-rectangular shape of the prepreg ribbon. The requirement of nonobviousness is met in that the non-rectangular towpreg ribbon unexpectedly promotes intimate lateral contact between adjacent composite tows allowing for good consolidation of a composite part. This application has not yet been examined.

6. Polyazomethines Containing Trifluoromethylbenzene Units

The claims of this application are directed to compositions of matter and article of manufacture. The novelty of the invention lies in the strutures of the polymers themselves. These polymers are used to prepare films, coatings, composites, and adhesives. The nonobviousness requirement is met by the properties of the polymers in that they are unexpectedly soluble and amorphous. In addition, they remain isotropic after thermal treatment.

A restriction requirement was placed on the application. The examiner stated that the claims in the application were directed to three different inventions: (1) polyazomethines; (2) copolyazomethines; and (3) articles made from polyazomethines. The claims to polyazomethines were elected to undergo prosecution first.

The examiner rejected the claims based on 35 U.S.C. §102(b) as anticipated by or, in the alternative, under 35 U.S.C. §103 as obvious over two references. Arguments were made establishing the differences in the properties of the polymers of the present invention as compared with those of the prior art.

7. Polyimides Containing the Pentafluorosulfanylbenzene Moiety

The claims of this application are directed to compositions of matter and articles of manufacture. The polyimides of the present invention may be used to prepare films, wire coating enamels, and semi-permeable membranes. The novelty requirement of the invention is met by the structures of the polyimides. The combination of high glass transition temperatures, high density, low solubility, and low dielectric properties render these compositions of matter nonobvious. This case has not yet undergone prosecution.

8. Apparatus for Providing a Uniform, Consolidated, Unidirectional, Continuous, Fiber-Reinforced Polymeric Material and Method Relating Thereto

This invention is classified as both a machine and a process invention. The novelty of the invention is found in the apparatus and the method which use a pre-melting chamber, a stationary bar assembly, and a loaded, cooled nip-roller apparatus to form a uniform, consolidated, unidirectional, continuous, filament-reinforced polymeric material. The nonobvious requirement is met in that the design of the present invention does not exhibit sensitivity to fiber jamming, processing rates for slurry powder coated polyimide thermoplastics have been vastly increased, and allowance is made for the expulsion of voids. This case has not yet undergone prosecution.

9. Poly(Arylene Ether-Co-Imidazole)s as Toughness Modifiers for Epoxy Resins

Claims in this application are directed to compositions of matter and articles prepared therefrom. The toughened epoxy resins may be used to prepare composites and molded parts. The novelty of the invention is found in the structures of the poly(arylene ether-co-imidazoles). By controlling the molecular weight, these polymers are soluble in epoxy at high concentrations. The nonobviousness requirement is met by the increase in the fracture tougheness of the epoxies prepared with the poly(arylene ether-co-imidazoles) by 1.75 fold over those of the prior art. This case has not yet undergone prosecution.

Notes for Chapter III

1. *In re Papesch*, 315 F.2d 381, 391, 137 U.S.P.Q. 43, 51 (C.C.P.A. 1963).

2. *In re Wetterau*, 148 U.S.P.Q. 499 (C.C.P.A. 1966).

CHAPTER IV

Summary

The work presented and discussed in this thesis shows that patent prosecution goes beyond the mere filing of an application. The United States patent system has a long evolutionary history and is constantly subject to change in order to meet the needs of the public. The patentability of an invention is subject to meeting the requirements set forth in Title 35 of the United States Code (35 U.S.C.), and the interpretations of these requirements are based on the rulings of the courts, especially the Supreme Court and the Court of Appeals for the Federal Circuit.

During the patent prosecution process, the claims which define an invention are argued in terms of meeting the requirements of patentability. The first requirement of patentability is that the subject matter of the invention must be classified as statutory subject matter in accordance with 35 U.S.C. §101, 161 and/or 171. If the subject matter of an invention is found to be non-statutory, there is no reason to pursue the filing of a patent application in the United States Patent and Trademark Office (PTO). Once the subject matter of an invention is classified as statutory subject matter, it must meet the technical requirements of novelty, utility, and nonobviousness as defined in 35 U.S.C. §102, 101, and 103 respectively.

The interpretation of these requirements is based on the decisions found in the case law. However, a study of the case law indicates that in some instances, there is not agreement as to how the law should be interpreted. This was illustrated in the case of *In re Dillon*, 919 F.2d 688, 16 U.S.P.Q.2d 1897 (Fed. Cir. 1990), *cert. denied*, 111 S. Ct. 1682 (1991) where in the dissent by Newman, J., joined by Cowen, Senior Circuit Judge, and Mayer, Circuit Judge the comment was made that the ruling of the en banc court changes what must be proved in order to patent a chemical compound or composition.

For inventions relating to the chemical arts, the inventor is often faced with rejections based on the obviousness of the invention in view of a combination of art (35 U.S.C. §103). These rejections are not always easily overcome, as the law requires that the applicant must make a showing to clearly distinguish the invention from the prior art. As was shown in Chapter III, the facts which surround each case are unique, and the strategy which is used to overcome the rejection of the claims is different for each case. Indeed, it can be concluded that arguing the requirements of patentability for inventions in the chemical arts is distinctly challenging.

APPENDIX

ISSUED PATENTS

US005245044A

United States Patent [19]

Connell et al.

[11] **Patent Number:** 5,245,044

[45] **Date of Patent:** Sep. 14, 1993

[54] DI(HYDROXYPHENYL)-BENZIMIDAZOLE MONOMERS

[75] Inventors: **John W. Connell; Paul M. Hergenrother**, both of Yorktown; **Joseph G. Smith**, Hampton, all of Va.

[73] Assignee: **The United States of America as represented by the Administrator of the National Aeronautics and Space Administration**, Washington, D.C.

[21] Appl. No.: **941,816**

[22] Filed: **Sep. 8, 1992**

Related U.S. Application Data

[62] Division of Ser. No. 790,730, Oct. 30, 1991.

[51] Int. Cl.⁵ C07D 235/18

[52] U.S. Cl. 548/305.7; 548/305.4; 548/145

[58] Field of Search 548/145, 328, 305.4, 548/305.7

[56] **References Cited**

PUBLICATIONS

Sues et al., "Light-Sensitive N-alkyl-2-, etc" CA 59:11505h/11506c (1963).
Kalle & Co. Akt. Ges. "Photosensitive Materials, etc" CA 55:20738a (1961).

Primary Examiner—Patricia L. Morris
Attorney, Agent, or Firm—George F. Helfrich

[57] **ABSTRACT**

Di(hydroxyphenyl)benzimidazole monomers were prepared from phenyl-4-hydroxybenzoate and aromatic bis(o-diamine)s. These monomers were used in the synthesis of soluble polybenzimidazoles. The reaction involved the aromatic nucleophilic displacement of various di(hydroxyphenyl)benzimidazole monomers with activated aromatic dihalides or activated aromatic dinitro compounds in the presence of an alkali metal base. These polymers exhibited lower glass transition temperatures, improved solubility, and better compression moldability over their commercial counterparts.

4 Claims, No Drawings

DI(HYDROXYPHENYL)-BENZIMIDAZOLE MONOMERS

ORIGIN OF THE INVENTION

The invention described herein was jointly made by employees of the U.S. Government and a contract employee in the performance of work under NASA Grant No. NAG1-448 and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the contractor has elected not to retain title.

This is a divisional of copending application Ser. No. 07/790,730 filed on Oct. 30, 1991.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to diol monomers. In particular, it relates to di(hydroxphenyl)benzimidazole monomers.

2. Description of the Related Art

Polybenzimidazoles (PBIs) are heterocyclic macromolecules commonly prepared by the condensation reaction of an aromatic bis(o-diamine) with an aromatic diacid or derivative thereof. These polymers possess high thermal, thermooxidative, and chemical stability; good mechanical properties; and excellent flame resistance, making them high-performance/high-temperature materials which are attractive for use in harsh environments. However, despite these properties, the processing of these polymers is somewhat difficult.

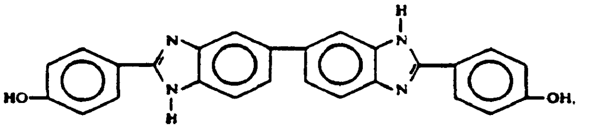
Buckley et al (*Encyclopedia of Polymer Science and Technology*, Volume 11, 2nd Ed., 1988, p. 572) review polybenzimidazoles. They specifically review poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole], which is commercially available primarily from Hoechst-Celanese Corporation. The processing of this material involves two steps: the formation of a foam which must be ground into a powder and reheating of the PBI powder. This polymer is mainly used in the formation of fibers because it is not very soluble in solvent. For example, in order to dissolve the PBI in dimethylacetamide (DMAc), both the solvent and the polymer had to be heated under pressure. The glass transition temperatures (Tg) of this polymer is 435° C. Because of this high Tg, the polymer is difficult to compression and injection mold.

Several methods have been used to prepare PBIs. Brinker and Robinson (U.S. Pat. No. 2,895,948) synthesized PBIs by reacting aliphatic dicarboxylic acids with aromatic bis(o-diamine)s. Vogel and Marvel (*Journal of Polymer Science*, 50, 511 (1961)) formed PBIs from the melt condensation of aromatic bis(o-diamine)s with aromatic diacids or derivatives thereof. Iwakura et al (*Journal of Polymer Science*, Part A, 2, 2605, (1964)) prepared PBIs in polyphosphoric acid. Hedberg and Marvel (*Journal of Polymer Science, Polymer Chemistry*, 12, 1823 (1974)) formed PBIs in sulfolane or diphenylsulfone from aromatic bis(o-diamine)s and aromatic diacids or derivatives thereof. Another preparative route by Higgins and Marvel (*Journal of Polymer Science*, Part A-1, 8, 171 (1970)) involves the reaction of aromatic bis(o-diamine)s with the bis(bisulfite adduct)s of dialdehydes. Packham et al (*Polymer*, 10 (12), 923 (1969)) formed PBIs from the alkoxide catalyzed reaction of aromatic bis(o-diamine)s with dinitriles. None of these methods teach the preparation of PBIs by the reaction of di(hydroxyphenyl)benzimidazole monomers with activated aromatic dihalide or dinitro compounds in the presence of an alkali metal base.

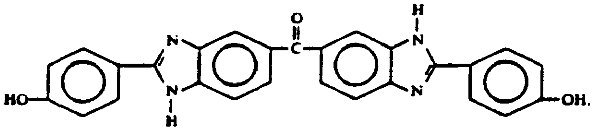
SUMMARY OF THE INVENTION

Several di(hydroxyphenyl)benzimidazole monomers were prepared from the reaction of phenyl-4-hydroxybenzoate with aromatic bis(o-diamine)s. These monomers have the following structural formulas:

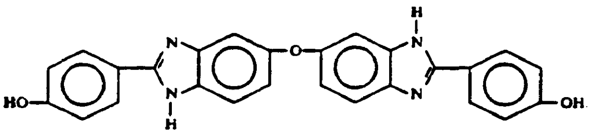
5,5'-Bis[2-(4-hydroxyphenyl)benzimidazole] a)



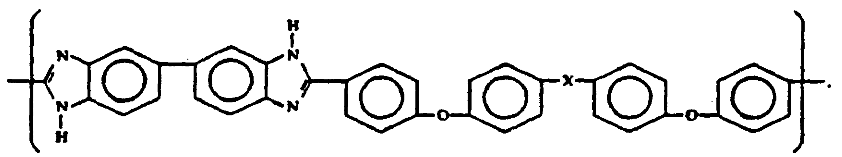
5,5'-Carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole] b)



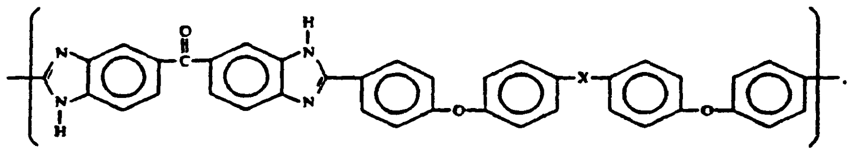
5,5'-Oxy-bis[2-(4-hydroxyphenyl)benzimidazole] c)



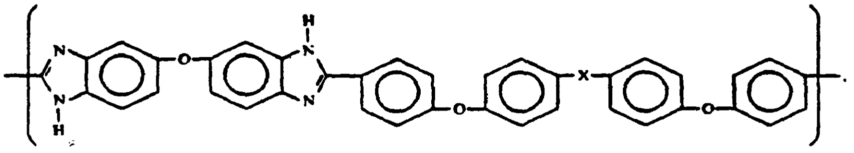
Soluble polybenzimidazoles (PBIs) were then prepared by the nucleophilic displacement reaction of these di(hydroxyphenyl)benzimidazole monomers with activated aromatic dihalide or dinitro compounds in the presence of an alkali metal base. The resulting PBIs had the following general structural repeat units:



a)

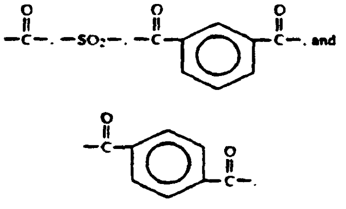


b)



c)

where x is

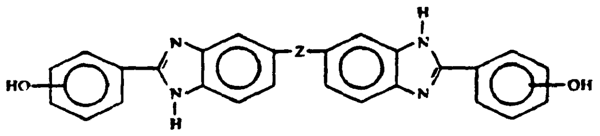


These polymers had glass transition temperatures (Tg) ranging from 264° to 352° C., much lower than their commercial counterparts which exhibited Tgs of 400° C. As a result of the lower Tgs, these polymers exhibited much better compression moldability than other PBIs. These polymers were found to be soluble in cold DMAc, as opposed to requiring hot DMAc and pressure to solubilize. The use of benzimidazole monomers to make PBIs proved to be more economical and easier to process than commercial PBIs without showing a loss in their physical and mechanical properties.

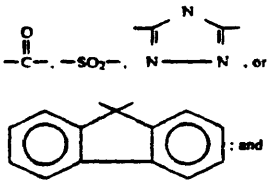
An object of the present invention is to prepare di(hydroxyphenyl)benzimidazole monomers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The synthesis of soluble PBIs involved the use of di(hydroxyphenyl)benzimidazole monomers. These monomers were prepared by reacting phenyl-4-hydroxybenzoate with various aromatic bis(o-diamine)s. These monomers have the following general structural formula:

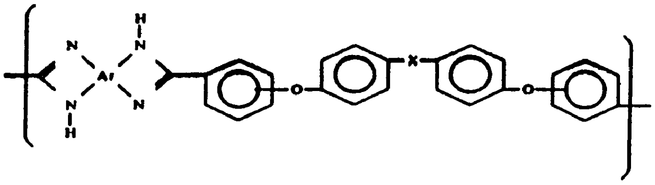


where z is either a direct bond, —CH_2—, —O—, —S—,



the catenation of the hydroxy groups may be meta-meta, para-para, or para-meta.

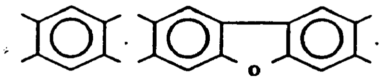
These benzimidazole monomers undergo a nucleophillic displacement reaction with activated aromatic dihalide or dinitro compounds in the presence of an alkali metal base such as: potassium carbonate, sodium carbonate, potassium hydroxide, and sodium hydroxide. The resulting PBIs are soluble in DMAc and have the following general structural repeat unit:

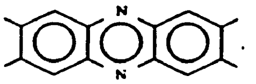


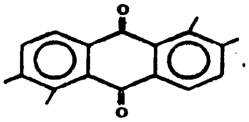
where:

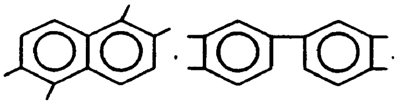
the catenation of oxygen is either meta-meta, para-para, or para-meta;

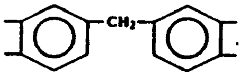
Ar is any one of the following:

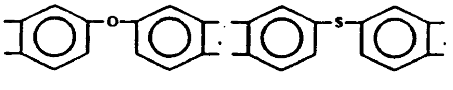


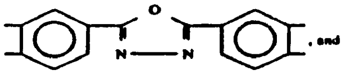












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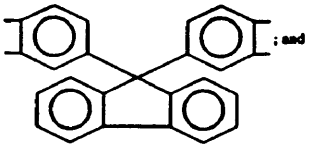
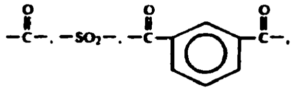
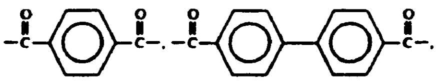
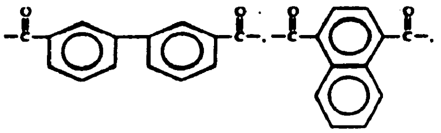
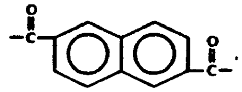


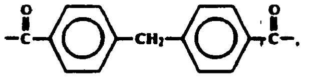
x is any one of the following:

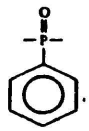


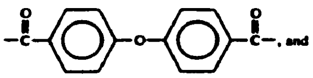


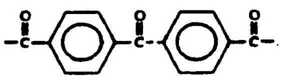












The solubility of these polymers allows for film formation, something which was difficult to achieve in previous PBI systems. These polymers also exhibited lower Tgs which makes compression and injection molding much easier.

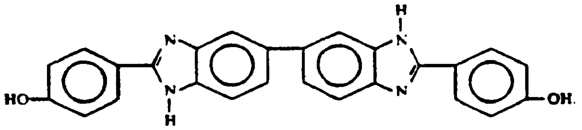
The following examples are illustrative of the invention.

EXAMPLE 1

Preparation of the di(hydroxyphenyl)benzimidazole monomers

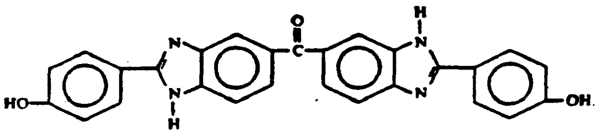
5,5'-Bis[2-(4-hydroxyphenyl)benzimidazole]

A mixture of 3,3',4,4'-tetraaminobiphenyl (commercially available from Hoechst-Celanese Corporation) (25.80 g, 0.120 mol), phenyl-4-hydroxybenzoate (commercially available from K and K Laboratories) (52.62 g, 0.246 mol), diphenylsulfone (95.30 g), and toluene (100 ml) was heated under a nitrogen atmosphere for 2.5 hours at 150° C. The toluene was removed and the temperature increased to 250° C. and maintained for 0.75 hour. The reaction mixture solidified to a yellow mass. A vacuum was subsequently applied and the temperature increased to 280° C. and maintained for 1.25 hours. The cooled brown reaction mixture was washed successively in hot acetone and toluene and subsequently dried at 110° C. to afford 48.90 g (97% crude yield) of a brown powder. The melting endothermic peak as determined by differential thermal analysis (DTA) at a heating rate of 10° C./min was 404° C. (sharp). The solid was recrystallized twice from N,N-dimethylacetamide (DMAc) using charcoal to afford a tan powder (28.37 g, 56% yield). The compound exhibited a broad endothermic peak by DTA with a minimum at 398° C. Analysis calcd. for $C_{26}H_{18}N_4O_2$: C, 74.63%; H, 4.34%; N, 13.39%. Found: C, 73.31%; H, 4.32%; N, 13.26%. The resulting monomer had the following structural formula:



5,5'-Carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole]

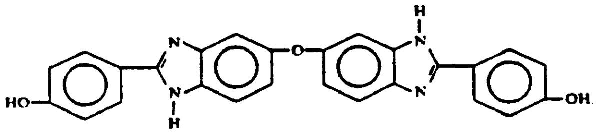
A mixture of 3,3',4,4'-tetraaminobenzophenone (commercially available from Burdick and Jackson) (22.61 g, 0.093 mol), phenyl-4-hydroxybenzoate (40.01 g, 0.187 mol), diphenylsulfone (110.45 g), and toluene (135 ml) was heated under a nitrogen atmosphere for 3 hours at 150° C. The toluene was removed and the temperature increased to 250° C. and maintained for 1.25 hours. A vacuum was subsequently applied and the temperature increased to 270° C. and maintained for 1 hour. The cooled yellow reaction mixture was washed successively in hot toluene and water and subsequently dried at 110° C. to afford 39.83 g (96% crude yield) of a yellow powder. The endothermic peak as determined by DTA was 387° C. (broad). The yellow solid was dissolved in DMAc, treated with activated charcoal, filtered, and poured into water to afford a yellow precipitate. The solid was dried under vacuum at 245° C. to afford 31.52 g (76% yield) of a brown powder. The endothermic peak as determined by DTA was 346° C. (broad). Analysis calcd. for $C_{27}H_{18}N_4O_3$: C, 72.64%; H, 4.06%; N, 12.55%. Found: C, 71.96%; H, 4.20%; N, 12.42%. The resulting monomer had the following structural formula:



5,5'-Oxy-bis[2-(4-hydroxyphenyl)benzimidazole]

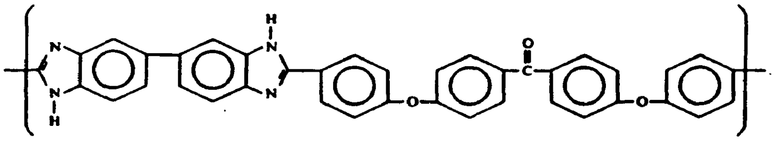
Oxydianaline was acetylated, nitrated, and the acetylated group hydrolyzed to give 3,3'-dinitro-4,4'-diaminodiphenyl ether. The 3,3'-dinitro-4,4'-diaminodiphenyl ether was then reduced with stannous chloride and hydrochloric acid to give bis(3,4-diaminophenyl)ether

A mixture of bis(3,4-diaminophenyl)ether (22.00 g, 0.096 mol), phenyl-4-hydroxybenzoate (41.00 g, 0.194 mol), diphenylsulfone (110.17 g), and toluene (135 ml) was heated under a nitrogen atmosphere for 3.5 hours at 150° C. The toluene was removed and the temperature increased to 250° C. and maintained for 1.5 hours. A vacuum was subsequently applied and the temperature increased to 280° C. and maintained for 1.25 hours. The cooled dark reaction mixture was washed in hot toluene and dried at 110° C. to afford 20.59 g (50% crude yield) of a dark purple powder. The dark solid was extracted with acetone to afford 12.39 g (30% yield) of a tan solid. The endothermic peak as determined by DTA was 317° C. (broad). Analysis calcd. for $C_{26}H_{18}N_4O_3$: C, 71.88%; H, 4.18%; N, 12.90%. Found: C, 71.91%; H, 4.22%; N, 13.06%. The resulting monomer had the following structural formula:



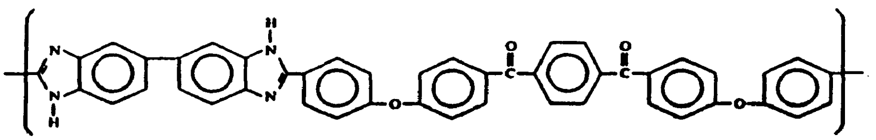
EXAMPLE 2

Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] (2.7835 g, 6.7 mmol), 4,4'-difluorobenzophenone (which is commercially available) (1.4515 g, 6.7 mmol), pulverized anhydrous potassium carbonate (2.4509 g, 17.7 mmol), dry DMAc (22 ml, 18% solids w/w), and toluene (50 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After 2.5 hours the viscous reaction mixture was diluted with 20 ml DMAc (9.7% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 25 ml DMAc (6.3% solids w/w) after 1.25 hours Stirring was continued for 10 minutes at 160° C. and then the reaction mixture cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a light brown polymer (3.60 g, 91% yield) with a Tg of 307° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.11 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23° C. of 22.8 ksi, 647 ksi, and 11.6%, respectively. Although the activated aromatic dihalide compound contained the halogen fluorine, a chlorine-containing compound may be substituted as is known in those skilled in the are. The resulting polymer had the following structural repeat unit:

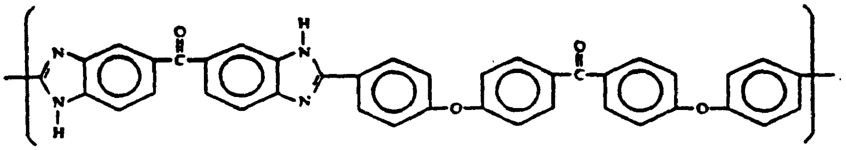


EXAMPLE 3

Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] (2.0392 g, 4.9 mmol), 1,3-bis(4-fluorobenzoyl)benzene (commercially available from Kennedy and Klin) (1.5707 g, 4.9 mmol), potassium carbonate (1.7379 g, 12.6 mmol), dry DMAc (18 ml, 18% solids w/w), and toluene (50 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After approximately 2 hours, the viscous reaction mixture was diluted with 21 ml DMAc (9.0% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 25 ml DMAc (5.7% solids w/w) after approximately 0.75 hour. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a light brown polymer (2.48 g, 73% yield) with a Tg of 276° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.99 dL/g. Unoriented thin films case from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23° C. of 19.4 ksi, 598 ksi, and 13.1% respectively. The resulting polymer had the following structural repeat unit:

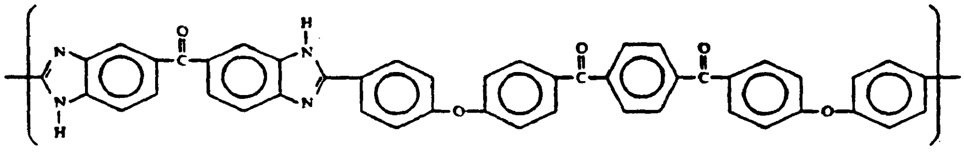


Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole] (2.5651 g, 5.7 mmol), 4,4'-difluorobenzophenone (1.2537 g, 5.7 mmol), pulverized anhydrous potassium carbonate (2.0686 g, 15.0 mmol), dry DMAc (18.5 ml, 18% solids w/w) and toluene (45 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After 1.75 hours the viscous reaction mixture was diluted with 18 ml DMAc (10% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 20 ml DMAc (6.7% solids w/w) after 0.25 hours. Stirring was continued for 0.5 hour at 160° C. and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a pale yellow polymer (3.03 g, 84% yield) with no observable Tg by differential scanning calorimetry. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 0.93 dL/g. The polymer had the following structural repeat unit:



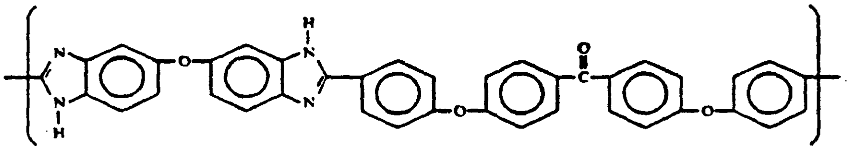
EXAMPLE 5

Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-carbonyl-bis[2-(4-hydroxyphenyl)benzimidazole] (2.5712 g, 5.8 mmol), 1,3-bis(4-fluorobenzoyl)benzene (1.8562 g, 5.8 mmol), pulverized anhydrous potassium carbonate (2.200 g, 15.9 mmol), dry DMAc (22 ml, 18% solids w/w), and toluene (50 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After approximately 1.1 hours the viscous reaction mixture was diluted with 20 ml DMAc (10% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 20 ml DMAc (7.0% solids w/w) after approximately 0.15 hour. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a pale yellow polymer (3.13 g, 75% yield) with a Tg of 264° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.43 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23° C. of 19.6 ksi, 612 ksi, and 5.6% respectively. The polymer had the following structural repeat unit:



EXAMPLE 6

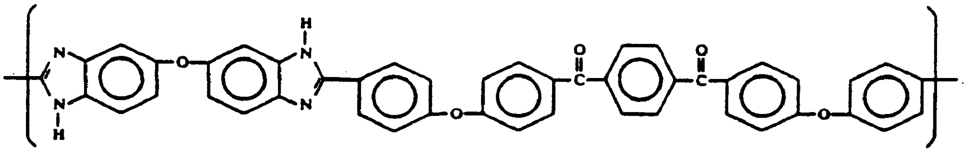
Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-oxy-bis[2-(4-hydroxyphenyl)benzimidazole] (2.9733 g, 6.8 mmol), 4,4'-difluorobenzophenone (1.4933 g, 6.8 mmol), pulverized anhydrous potassium carbonate (2.4468 g, 17.7 mmol), dry DMAc (21.5 ml, 18% solids w/w), and toluene (45 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After approximately 3 hours the viscous reaction mixture was diluted with 20 ml DMAc (10% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 25 ml DMAc (6.7% solids w/w) after approximately 1.5 hours. Stirring was continued for 0.25 hour at 160° C. and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a white polymer (3.60 g, 84% yield) with a Tg of 294° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.34 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23° C. of 19.7 ksi, 576 ksi, and 7.0%, respectively. The resulting polymer had the following structural repeat unit:



EXAMPLE 7

Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer mechanical stirrer, and Dean Stark trap was placed 5,5'-oxy-bis[2-(4-hydroxyphenyl)benzimidazole] (2.3330 g, 5.4 mmol), 1,3-bis(4-fluorobenzoyl)benzene (1.7308 g, 5.4 mmol), pulverized anhydrous potassium carbonate (1.9948 g, 14.1 mmol), dry DMAc (19.5 ml, 18% solids w/w), and toluene (45 ml). The mixture was heated to 140°-150° C. for 3.5 hours and then heated to 155°-160° C. After approximately 1 hour the viscous reaction mixture was diluted with 20 ml DMAc (9.9% solids w/w) and stirring continued at 155°-160° C. The viscous reaction mixture was diluted with 20 ml DMAc (6.8% solids w/w) after approximately 0.3 hour. Stirring was continued for 5 minutes and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110° C. to provide a white polymer (3.13 g, 75% yield) with a Tg of 269° C. The inherent viscosity of a 0.5% solution in DMAc at 25° C. was 1.79 dL/g. Unoriented thin films cast from a

DMAc solution gave tensile strength, tensile modulus, and elongation at 23° C. of 18.4 ksi, 591 ksi, and 6.1%, respectively. The resulting polymer had the following structural repeat unit:

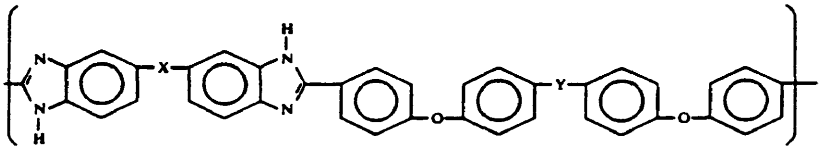


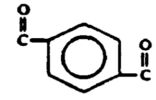
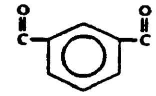
Although these polymers were made using DMAc as the solvent, other solvents known to those skilled in the art, such as N-methylpyrrolidinone, diphenylsulfone, and sulfolane may also be used.

In addition to the polymers made in the foregoing examples, additional polymers were made and their properties are tabulated in Tables 1 and 2.

TABLE 1

POLYMER CHARACTERIZATION



Y	X	ηinh.[1] dL/g	Tg.[2] °C.	Temp. of 5% wt. loss. °C.[3] air	Temp. of 5% wt. loss. °C.[3] N2
SO_2	nil	1.87	352	441	456
	O	1.42	322	435	451
	CO	0.93	N.D.[4]	422	433
$\overset{\text{O}}{\overset{\|}{\text{C}}}$	nil	1.11	307	466	502
	O	1.34	294	442	489
	CO	0.93	N.D.[4]	433	451
	nil	1.19	295	469	520
	O	1.23	282	469	490
	CO	0.79	276	444	478
	nil	1.99	276	476	515
	O	1.79	269	454	499
	CO	1.43	264	467	489

[1] Inherent viscosity measured in DMAc on 0.5% (w/v) solutions at 25° C.

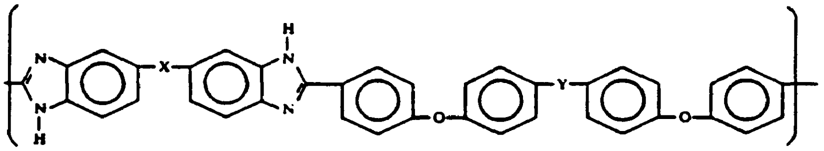
[2] Glass transition temperature determined by DSC at a heating rate of 20° C./min

[3] TGA measured on powdered samples at a heating rate of 2.5° C./min after preheat sample to 180°C. and holding for 0.5 h before analysis

[4] Not detected

TABLE 2

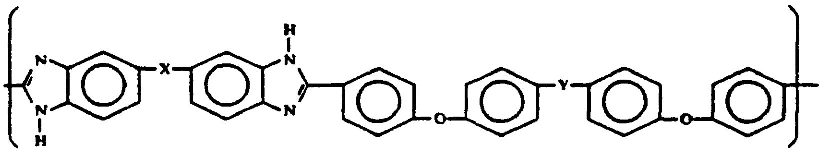
UNORIENTED THIN FILM
TENSILE PROPERTIES AT 23° C.*

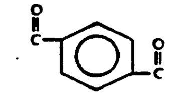
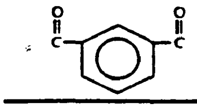


Y	X	ηinh. dL/g	Strength. ksi	Modulus. ksi	Elong. at break. %
SO_2	nil	1.87	22.5	652	9.3
	O	1.42	18.8	569	7.6

TABLE 2-continued

UNORIENTED THIN FILM
TENSILE PROPERTIES AT 23° C.*

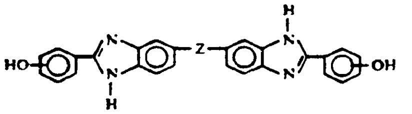


Y	X	ηinh. dL/g	Strength. ksi	Modulus. ksi	Elong. at break, %
$\overset{O}{\overset{\|}{C}}$	nil	1.11	22.8	647	11.6
	O	1.34	19.7	576	7.0
	nil	1.19	20.2	605	14.3
	O	1.23	17.6	539	18.0
	nil	1.99	19.4	598	13.1
	O	1.79	18.4	591	6.1
	CO	1.43	19.6	612	5.6

*Films dried at 100, 200, and ~50° C above their respective Tg in an air oven

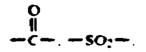
What is claimed is:

1. A di(hydroxyphenyl)benzimidazole monomer having the following structure:



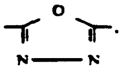
where z is a direct bond or is selected from the group consisting of:

—CH$_2$—, —O—, —S—,

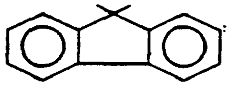


$$-\overset{O}{\overset{\|}{C}}-,\ -SO_2-,$$

-continued



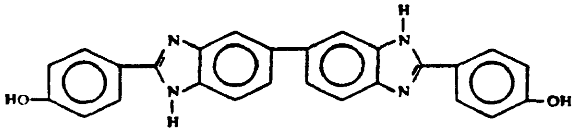
, and



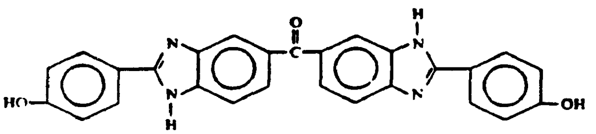
; and

the catenation of the hydroxy groups is selected from the group consisting of: meta-meta, para-para, and para-meta.

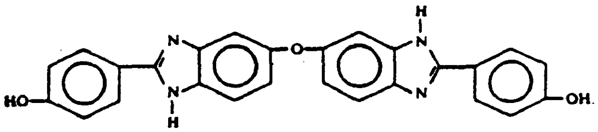
2. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:



3. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:



4. The di(hydroxyphenyl)benzimidazole monomer of claim 1, having the following structural formula:


HO
N
N
H
O
H
N
N
OH.

US005248519A

United States Patent [19]

Stoakley et al.

[11] **Patent Number:** **5,248,519**
[45] **Date of Patent:** **Sep. 28, 1993**

[54] PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A SOLUBLE POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE

[75] Inventors: **Diane M. Stoakley; Anne K. St. Clair,** both of Poquoson, Va.

[73] Assignee: **The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.**

[21] Appl. No.: **736,667**

[22] Filed: **Jul. 26, 1991**

[51] **Int. Cl.**^{5} **B05D 1/00; B05D 5/06; B05D 5/12**

[52] **U.S. Cl.** 427/96; 427/163; 427/385.5; 427/388.1

[58] **Field of Search** 427/384, 385.5, 388.1, 427/255.6, 96, 163; 528/322; 524/507

[56] **References Cited**

U.S. PATENT DOCUMENTS

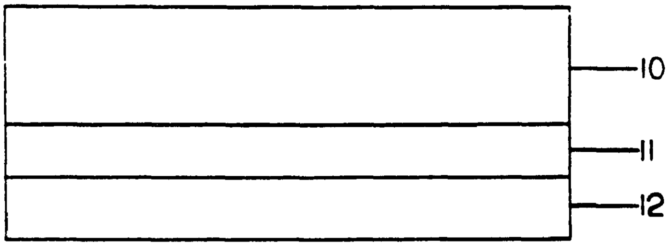
4,558,117	12/1985	Nakano et al.	528/184
4,574,056	3/1986	Kimura	252/514
4,996,293	2/1991	Tsuyoshi	528/352
5,037,862	8/1991	Nishizawa et al.	523/223
5,041,513	8/1991	Okinoshima et al.	528/10

Primary Examiner—Shrive Beck
Assistant Examiner—Bret Chen
Attorney, Agent, or Firm—George F. Helfrich

[57] ABSTRACT

An assembly of an article and a polyimide is prepared. The assembly resists dimensional change, delamination, or debonding when exposed to changes in temperature. An article is provided. A soluble polyimide resin solution having a low coefficient of thermal expansion (CTE) was prepared by dissolving the polyimide in solvent and adding a metal ion-containing additive to the solution. Examples of this additive are: $Ho(OOCCH_3)_3$, $Er(NPPA)_3$, $TmCl_3$, and $Er(C_5H_7O_2)_3$. The soluble polyimide resin is combined with the article to form the assembly.

11 Claims, 1 Drawing Sheet



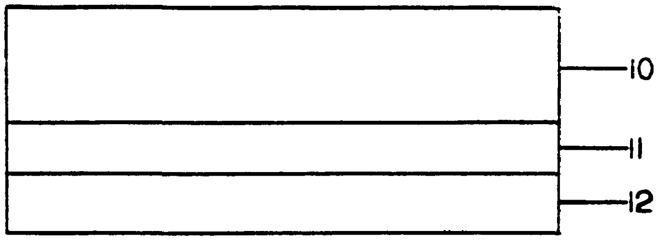


FIGURE 1

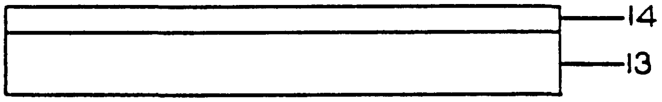


FIGURE 2

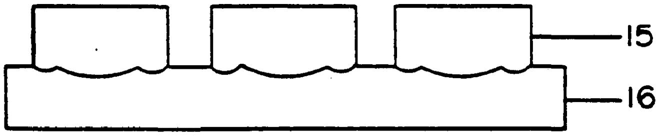


FIGURE 3

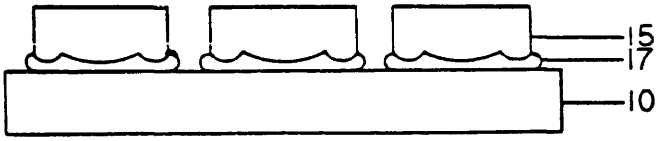


FIGURE 4

PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A SOLUBLE POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the U.S. Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

CROSS REFERENCE TO RELATED CASES

This application is related to co-pending patent application Ser. No. 07/736,880, filed Jul. 26, 1991, entitled "A Process for Preparing an Assembly of an Article and a Polyimide which resists Dimensional Change, Delamination, and Debonding when Exposed to Changes in Temperature".

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to soluble polyimides which have a low coefficient of thermal expansion (CTE). More particularly, it relates to the preparation of an assembly of an article and a soluble polyimide which resists dimensional change, delamination, and debonding when exposed to changes in temperature.

2. Description of the Related Art

Polyimides have become widely used as high performance polymers as a result of their excellent thermal stability and toughness. However, polymers in general, including polyimides, have higher CTEs than metals, ceramics, and glasses. Lowering the CTE of polyimides would increase their usefulness for aerospace and electronic applications where dimensional stability is a requirement.

The CTEs of polyimides have been lowered in the past by linearizing the polymer molecular structure or by controlling the orientation of the polyimide film. Numata et al. (*Polymer Engineering and Science*, 28, (4), 906 (1988)) lowered the CTE by synthesizing a linear polyimide. By employing polyimides prepared from pyromellitic dianhydride (PMDA) or 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and aromatic diamines that contain only benzene or pyridine rings in para-positions without flexible linkages, they have synthesized polyimides with CTEs from 20–0.4 ppm/°C. Numata and Miwa (*Polymer*, 30, (60), 1170 (1989)) found that the CTEs of uniaxially stretched polyimide films with rigid and flexible molecular chains were lower than their non-oriented counterparts.

By the present invention, an assembly of an article and a soluble polyimide with a reduced CTE is prepared. The assembly resists dimensional change, delamination, and debonding when exposed to changes in temperature. The CTEs have been lowered by incorporating a metal ion-containing additive into a soluble polyimide. St. Clair et al. (U.S. Pat. No. 4,284,461), Taylor et al. (U.S. Pat. No. 4,311,615) and Stoakley and St. Clair ("Lanthanide-Containing Polyimides" *Recent Advances in Polyimide Science and Technology*, W. D. Weber and M. R. Gupta, Eds., Society of Plastics Engineers, New York, 1987, pp 471–479) used these additives to alter the adhesive, electrical, and magnetic properties of polyimides.

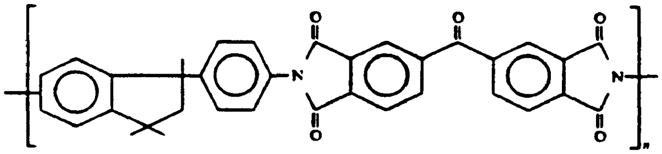
Accordingly, it is the object of the present invention to prepare an assembly of an article and a soluble polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes by adding a metal ion-containing additive to a soluble polyimide.

Another object of the invention is to reduce the CTE of the polyimide so it more closely matches the CTE of the article by incorporating a metal ion-containing additive into the soluble polyimide.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

SUMMARY OF THE INVENTION

An assembly of an article and a polyimide is prepared. The assembly resists dimensional change, delamination, or debonding when exposed to changes in temperature. An article is provided. A polyimide resin having a reduced CTE was prepared by dissolving, for example, XU-218 ® polyimide powder of the structure:



into N,N-dimethylacetamide (DMAc) to which a metal ion-containing additive was added. Examples of this additive are: holmium acetate $Ho(OOCCH_3)_3$, erbium N-phenylphthalamate $Er(NPPA)_3$, thulium chloride $TmCl_3$, and erbium acetylacetonate $Er(C_5H_7O_2)_3$. The resin is combined with the article to form the assembly.

The article selected for the assembly is: a solar concentrator, antennae, solar cell arrays, second surface mirrors, precision solar reflectors, electronic circuit boards, or any other item known to those skilled in the art. A precision solar reflector is the preferred article for this application.

A solution of the soluble polyimide was prepared by dissolving Ciba Geigy's XU-218 ® polyimide powder in chloroform, DMAc or any other suitable organic solvent. A metal ion-containing additive was then added to the solution. Erbium acetylacetonate gave the best results.

An article is either coated with or embedded into the soluble polyimide solution or bonded to a polyimide substrate. In cases where the article is coated with or embedded into the soluble polyimide, heat was used to remove the excess solvent. The solvent was removed by heating the solution to about 100° C.–300° C. The polyimide substrate is formed by casting the soluble polyimide solution into a mold and heating to about 100° C.-300° C. prior to the attachment of an article. The article is bonded to the polyimide substrate with a polyimide-based adhesive or by surface treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing a preferred embodiment of the present invention where the low CTE polyimide is used as a substrate.

FIG. 2 is a schematic showing an article which is coated with a low CTE polyimide to form an assembly.

FIG. 3 is a schematic showing the formation of an assembly by embedding an article into the low CTE polyimide.

FIG. 4 is a schematic showing an article attached to a low CTE polyimide substrate with an adhesive.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A polyimide resin solution, which had a low coefficient of thermal expansion (CTE), was prepared at 15% solids. Ciba Geigy's XU-218® polyimide powder was dissolved in DMAc to yield a polyimide resin that was 15% solids. A metal ion-containing additive was added at a concentration range of approximately 4-30 weight percent to the polyimide resin.

The metal ion-containing polyimide resin was cast as a film on soda-lime glass plates using a doctor blade set to a wet film thickness of approximately 18 mil. The film was placed in a low humidity box overnight and was then heated in a forced air oven for 1 hour each at 100°, 200°, and 300° C. to effectively remove the DMAc solvent. The film was removed from the glass plate by soaking in water.

Another soluble polyimide was prepared from the reaction of an equimolar quantity of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) with 1,3-bis(aminophenoxy)benzene (APB) in a polar organic solvent such as N,N-dimethylacetamide (DMAc). Once the polyamic acid was formed, acetic anhydride and pyridine were added to chemically imidize the acid. The polyimide was precipitated, recovered, washed with water, dried, and redissolved in solvent such as DMAc to form the imide solution.

In addition to the soluble polyimides used, other soluble polyimides known to those skilled in the art may also be used in the present invention.

Although DMAc was the solvent used for this application, other solvents such as chloroform, methyl ethyl ketone, and isobutyl ketone could also be used.

The metal ion-containing additives of this invention included: holmium acetate $Ho(OOCCH_3)_3$, erbium N-phenylphthalamate $Er(NPPA)_3$, thulium chloride $TmCl_3$, and erbium acetylacetonate $Er(C_5H_7O_2)_3$. Each additive reduced the CTE and it was found that $Er(C_5H_7O_2)_3$ gave the best results. The data is shown in Table I.

TABLE I

Coefficients of Thermal Expansion of Metal Ion-Containing Polyimide Films

Additive	% Additive	Tg by TMA, °C.	CTE ppm/°C.
XU-218 ® Control	0.0	320	46.1
$Ho(OOCCH_3)_3$	13.4	329	34.7
$Er(NPPA)_3$	28.6	291	30.7
$Er(C_5H_7O_2)_3$	17.3	325	28.3

A low CTE polyimide substrate is prepared by pouring the soluble polyimide resin into a mold and heating for one hour each at 100°, 200°, and 300° C. to remove the solvent.

An article is provided to form an assembly with the polyimide. Examples of this article are: a solar concentrator, antennae, solar cell arrays, second surface mirrors, precision solar reflectors, or electronic circuit boards. Other articles known to those skilled in the art can also be used. A polyimide solution having a low CTE is prepared. The solution is used to coat the article, to embed the article, or to form a substrate to which the article is attached. For example, a circuit board is coated by either spraying, dipping, or brushing with the polyimide solution. The solution is heated for 1 hour each at 100°, 200°, and 300° C. in a forced air oven to remove the excess solvent. The coated article is resistant to delamination when exposed to temperature changes.

In another example, the polyimide solution is cast into a mold. The circuit board is embedded into the solution prior to heating. After heating, the resulting assembly is resistant to debonding.

As yet another example, an article is attached to a polyimide substrate formed from the polyimide solution. The soluble polyimide is poured into a mold and is heated to remove the excess solvent. The article is attached to the substrate with a polyimide-based adhesive. The resulting assembly is resistant to debonding and delamination when exposed to changes in temperature.

In yet another example, a thin-film assembly for a precision solar reflector is prepared. The soluble polyimide solution containing the metal ion additive is poured onto a glass, metal, or other surface having the shape of the reflector. The resin is spun-cast to 0.5-5.0 mil thickness and heated to produce a low CTE polyimide film. The polyimide film is combined with a reflecting layer and a protective topcoat to form the assembly.

EXAMPLES

Example 1

A solution of XU-218® in DMAc was prepared by dissolving 1.66 g of XU-218® polyimide powder into 9.40 g DMAc to yield a polyimide resin that was 15% solids. A film was cast that was 18 mil wet and left in a low humidity film box overnight. The film was heated in a forced air oven for 1 hour each at 100° C., 200° C., and 300° C. to effectively remove the DMAc solvent. The resulting XU-218® control film was a transparent yellow film with a Tg of 326° C. and CTE of 46.1 ppm/° C. An XU-218® solution was prepared as described above to which 0.257 g (0.00075 moles) $Ho(OOCCH_3)_3$ was added and stirred for several hours. A film was cast and cured as in the case of the control film. The resulting 1:4 $Ho(OOCCH_3)_3$:XU-218® film had a Tg of 329° C. and CTE of 34.7 ppm/° C.

Example 2

An XU-218® solution was prepared by the process of Example 1 but the heating schedule was altered to 1 hour at 100° C., 1-½ hours at 200° C., and 2 hours at 250° C. The resulting transparent yellow control film had a Tg of 320° C. and a CTE of 46.1 ppm/° C. An XU-218® solution was prepared by the process of Example 1 to which 0.665 g (0.00075 moles) $Er(NPPA)_3$ was added and stirred for several hours. A film was cast and heated by the process above. The resulting 1:4 Er(NPPA)$_3$:XU-218® film was transparent yellow and had a Tg of 291° C. and CTE of 30.7 ppm/° C.

Example 3

The process of Example 2 was repeated using 0.348 g (0.00075 moles) Er($C_5H_7O_2$)$_3$. The resulting 1:4 Er($C_5H_7O_2$)$_3$:XU-218® film was transparent amber and had a Tg of 325° C. and CTE of 28.3 ppm/° C.

Example 4

A circuit board 13 (of FIG. 2) is coated with a low CTE polyimide resin solution 14 (of FIG. 2) as in Example 1. The coating is applied to the circuit board by spraying, brushing, dipping, or any other method known to those skilled in the art. The solvent is removed by heating for 1 hour each at 100° C., 200° C., and 300° C. in a forced air oven. The coated article is resistant to delamination when exposed to changes in temperature.

Example 5

An article 15 (of FIG. 3) is attached to a low CTE polyimide substrate prepared from the soluble polyimide solution as in Example 1. The solution is poured into a mold and the article is embedded 16 (of FIG. 3) in the solution. The assembly is heated for 1 hour each at 100° C., 200° C., and 300° C. in a forced air oven to remove the solvent. The article is resistant to debonding when exposed to changes in temperature.

Example 6

An article 15 (of FIG. 4) is attached to a low CTE polyimide substrate prepared from the soluble polyimide solution 10 (of FIG. 4) as in Example 1. The solution is poured into a mold and is heated for 1 hour each at 100° C., 200° C., and 300° C. in a forced air oven to remove the solvent. The article is attached to the substrate by bonding it with an adhesive 17 (of FIG. 4). The article is resistant to debonding when exposed to changes in temperature.

Example 7

A thin-film assembly for a precision solar reflector is prepared (FIG. 1). A soluble polyimide resin solution as in Example 1 was prepared. The solution is poured onto a glass, metal, or other surface which has the shape of the reflector. The solution is spun-cast to a thickness of 0.5-5.0 mils and heated to 100°-300° C. in a forced air oven. The resulting substrate 10 (of FIG. 1) is removed from the surface and is metallized with a highly reflecting metal layer 11 (of FIG. 1) such as silver, aluminum, or chromium. The metal layer is applied at a thickness between 10 and 2000 Å using a surface treatment such as vapor deposition or sputtering. A clear protective topcoat 12 (of FIG. 1) is applied at 0.1-1.0 mil thickness to prevent tarnishing. The layers of the assembly are resistant to dimensional change, debonding, or delamination upon exposure to changes in temperature.

Example 8

A low CTE soluble polyimide was prepared by reacting an equimolar quantity of APB and 6FDA in DMAc. Acetic anhydride and pyridine are added to the resulting polyamic acid solution. The polyimide precipitate was recovered, washed with water, and dried. The imide powder was dissolved in DMAc to form a solution and TmCl$_3$ was added at a concentration of 1:5 TmCl$_3$:APB/6FDA. The solution was cast on a glass plate and was placed in a low humidity film box overnight and heated to effectively remove the DMAc solvent. The resulting film had a CTE of 38.4 ppm/° C. as compared to the control film of 51.0 ppm/° C.

The above examples are considered to be illustrative of the invention and there may be modifications and variations in the metal ion-containing additive, the soluble polyimide, or the article that will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth herein. It is therefore to be understood that the invention may be practiced otherwise than as specifically described and claimed herein.

What is claimed to be new and desired to be secured by Letters Patent of the United States is:

1. A process for preparing an assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes, the process comprising:

a. providing an article;

b. preparing a solution of a soluble polyimide resin with a reduced coefficient of thermal expansion by dissolving a soluble polyimide resin in a solvent selected from the group consisting of N,N-dimethylacetamide (DMAc), chloroform, methyl ethyl ketone, and isobutyl ketone to make said solution;

c. adding a metal ion-containing additive selected from the group consisting of Ho(OOCCH$_3$)$_3$, Er(NPPA)$_3$, TmCl$_3$, and Er($C_5H_7O_2$)$_3$ to form a metal ion-containing solution; and

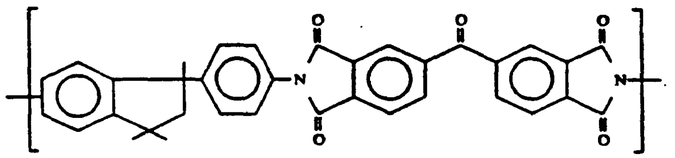
d. heating the said metal ion-containing solution and combining it with the article to form the assembly.

2. The process of claim 1, wherein said article is selected from the group consisting of solar concentrators, antenna, solar cell arrays, second surface mirrors, precision solar reflectors, and electronic circuit boards.

3. The process of claim 2, wherein said article is a precision solar reflector.

4. The process of claim 1, wherein the concentration of said soluble polyimide resin is about 10-15 weight percent of the said metal ion-containing solution.

5. The process of claim 1, wherein said polyimide has the repeat unit:



6. The process of claim 1, wherein said solvent is selected from the group consisting of N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-

pyrrolidone, dimethylsulfoxide, and bis(2-methoxyethyl)ether.

7. The process of claim 6, wherein said solvent is N,N-dimethylacetamide.

8. The process of claim 1, wherein the concentration of said metal ion-containing additive is 4–30 weight percent of the said metal ion-containing solution.

9. The process of claim 1, wherein said metal ion-containing additive is $Er(C_5H_7O_2)_3$.

10. The process of claim 1, wherein said metal ion-containing solution is used to coat the article prior to heating for solvent removal.

11. The process of claim 1, wherein said soluble polyimide resin is made from 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride and 1,3-bis(aminophenoxy)benzene.

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[54] PREPARING POLYMERIC MATRIX COMPOSITES USING AN AQUEOUS SLURRY TECHNIQUE

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[51] **Int. Cl.^{5}** **C09J 5/02**
[52] **U.S. Cl.** **156/307.4**; 156/330.9; 428/367; 428/408; 524/538; 524/608
[58] **Field of Search** 524/538, 608; 156/330.9, 307.4; 428/367, 408

[56] References Cited

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4,169,860	10/1979	von Bonin et al.	524/538
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[57] **ABSTRACT**

An aqueous process was developed to prepare a consolidated composite laminate from an aqueous slurry. An aqueous poly(amic acid) surfactant solution was prepared by dissolving a poly(amic acid) powder in an aqueous ammonia solution. A polymeric powder was added to this solution to form a slurry. The slurry was deposited on carbon fiber to form a prepreg which was dried and stacked to form a composite laminate. The composite laminate was consolidated using pressure and was heated to form the polymeric matrix. The resulting composite laminate exhibited high fracture toughness and excellent consolidation.

11 Claims, No Drawings

PREPARING POLYMERIC MATRIX COMPOSITES USING AN AQUEOUS SLURRY TECHNIQUE

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to composite materials. In particular, it relates to an aqueous process to prepare carbon fiber/polymer powder prepregs using an aqueous slurry technique.

2. Description of the Related Art

High temperature polymeric thermoplastic resins are attractive to the aerospace industry because of their excellent mechanical properties which are retained over a wide temperature range. The beneficial properties of such polymers as polyimides include strength, toughness and adhesion which makes them prime candidates as matrix resins in advanced carbon-fiber reinforced composites. However, preparing composites of these materials has been difficult due to their lack of melt flow and insolubility in standard solvents. Successful composite manufacture must be preceded by a pre-impregnation step in which the resin is intimately impregnated into the carbon fibers so as to require minimal melt flow to achieve composite consolidation.

Various techniques have been developed to combine thermoplastic resins and reinforcing fibers to form prepreg materials. In these techniques, polymer is deposited on the fiber from the melt state, from solution, or in powder form from a slurry or a fluidized bed. Many thermoplastic resins, such as polyimides, have poor melt flow and are insoluble in most solvents but may be prepared in powder form.

Dyksterhouse et al (U.S. Pat. No. 4,894,105) formed composites by dispersing polymer particles in an aqueous medium containing an effective amount of a dissolved polymeric binding agent. This binding agent is polyacrylic acid. The viscosity of the medium must be at least 50,000 cps to form a gelled impregnation bath wherein the polymer particles are uniformly suspended. This viscosity requirement is significantly higher than the present invention, where the viscosity is only 300 cps.

Pike (U.S. Pat. No. 4,480,088) teaches a process to prepare water soluble polyimide resin systems. This process involves the formation of the poly(amic acid) salt which may be converted to the polyimide by heating. There is no mention of the use of the poly(amic acid) salt as a surfactant for polymeric powders in an aqueous system.

Neither of the two previously mentioned inventions teaches the process for preparing a consolidated composite laminate using a poly(amic acid) salt as a surfactant. By the present invention, there is no need to increase the viscosity of the aqueous medium as was required in the related art. Also, the use of the poly(amic acid) as a surfactant allows for better compatibility throughout the final composite.

SUMMARY OF THE INVENTION

An aqueous process was developed for preparing uniform and processable consolidated composite laminates from polymers which are difficult to process. Examples of these polymers include polyimides, poly(aryleneethers), polysulfones, polybenzimidazoles, and liquid crystalline polymers. The process utilizes conventional solution prepregging techniques but does not require organic solvents, nor does it incorporate secondary polymers which are so chemically dissimilar to the primary polymer that there is incompatibility in the final product.

In the present invention, an aqueous poly(amic acid) surfactant solution was prepared by forming the base salt of the poly(amic acid). This was achieved by mixing a poly(amic acid) powder with an aqueous ammonia solution. The resulting solution had a viscosity of less than 300 cps. An aqueous slurry of 5-20% solids was formed from this solution by adding a polymeric powder. This slurry was deposited onto carbon fiber using standard wet prepregging techniques. The prepreg was dried at room temperature to remove excess water leaving the poly(amic acid) salt which binds the polymer to the fiber. The prepreg was then further dried in a forced air oven and partially imidized. The dried prepreg was stacked to form a composite laminate which was molded under heat and pressure. The application of heat and pressure imparts melt flow in the polymer and completes imidization of the poly(amic acid) salt forming a polymer blend. The resulting composite laminate exhibited high fracture toughness and excellent consolidation.

An object of the present invention is to develop an aqueous process for preparing consolidated composite laminates.

Another object of the present invention is to prepare a low viscosity aqueous poly(amic acid) surfactant solution.

Another object of the present invention is to prepare a slurry from the low viscosity poly(amic acid) surfactant solution and a polymeric powder.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the formation of the aqueous poly(amic acid) surfactant solution, any poly(amic acid) precursor may be used so long as it may be rendered water soluble and converted to the polyimide by the application of heat. Ammonia is recommended as the solubilizing base because it may be readily removed in subsequent steps of composite fabrication. The concentration of poly(amic acid) in water should be as low as possible but high enough to effectively disperse the polymeric powder in the slurry and to bind the polymeric powder to the fiber in the dried prepreg. This concentration is around 3%. It was found that when the concentration was too high, resin melt flow was inhibited. However, at low concentrations, the polymeric powder could not be well-dispersed. Although increased viscosity will enhance the stability of the slurry, it was found that at a 3% poly(amic acid) salt concentration, a viscosity of 300 cps or less effectively suspended the polymeric powder.

The polymeric powder should be of a fine particle size to allow for easy dispersion. It is desirable that the median particle size be equal to or smaller than the diameter of the fibers to be impregnated. This promotes more uniform penetration. The concentration of the polymeric powder should be at a maximum but sufficient fluidity should be retained to impregnate the fibers. It was found that this concentration ranged from 5-20% solids.

The fibers may be impregnated with the aqueous slurry by passing fiber tows through a dip tank containing the slurry. The resulting prepreg material may be air-dried to remove excess water and allow for the poly(amic acid) salt to act as a binding agent between the polymer powder and the fiber. The use of a forced-air oven will remove not only any remaining water but will thermally imidize the poly(amic acid) salt, driving off the ammonia.

The prepreg can be stacked to form a composite laminate which is molded under heat and pressure. The application of heat and pressure imparts melt flow in the polymer and completes imidization of the poly(amic acid) salt resulting in a polymer blend. It was found that a pressure setting of 1000 psi resulted in complete consolidation of the laminate over greater than 90% of their areas. The composite laminates also exhibited high fracture toughness in addition to excellent consolidation.

The following examples are illustrative of the invention.

EXAMPLE I

Composites of LARC TM -TPI polyimide. commercially available from Mitsui Toatsu Chemicals. and Hercules AS-4 carbon fiber were prepared in the following manner. LARC TM -TPI 1500 pre-imidized powder (high flow grade) was obtained from Mitsui Toatsu Chemicals. The as-received powder had a median particle diameter of 23 μm. LARC TM -TPI poly(amide acid) (PAA) powder was also obtained from Mitsui Toatsu Chemicals. The PAA powder was received as a coarse powder and was ground finer to reduce the time required to dissolve it.

To formulate the LARC TM -TPI slurry, a basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then. 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Finally, 350.5 g of LARC TM -TPI 1500 pre-imidized powder was dispersed into the solution resulting in a stable slurry containing approximately 20% solids polymer with a 7.5:1 ratio of pre-imidized powder to PAA (based on the imide form of the PAA).

The polyimide slurry was deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow was pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup was controlled using a die of fixed gap at the dip tank exit. The fiber was taken up on a drum that had a diameter of 61 cm. The resulting prepreg had a fiber areal weight of approximately 140 g/m^2. The prepreg was air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites were formed by stacking prepreg plies between Kapton® film, available from DuPont, coated with a release agent in a matched-metal

mold. The moldings were carried out in a heated hydraulic press. Panels were fabricated at molding pressures of 1000 psi. A series of temperature ramps and holds was used to prevent the PAA molecular weight from increasing too rapidly and hindering melt flow. The heating ramps were fixed at 5.6° C./min. The isothermal holds were as follows. 260° C. for 75 minutes. 288° C. for 45 minutes. 302° C. for 90 minutes. and finally 371° C. for 60 minutes.

Panels were ultrasonically scanned at a sensitivity level sufficient to detect microvoids in standard epoxy/-graphite composites. All panels had C-scans showing complete consolidation over greater than 90% of their areas. Short beam shear properties were measure according to ASTM D234472 (4:1 span-to-depth ratio) and flexure properties according to ASTM D79066 (32:1 span-to-depth ratio). Mode 1 composite fracture toughness (G_{IC}) was obtained by the double cantilever beam (DCB) test on a unidirectional laminate with Kapton® film placed at the mid-plane to control crack initiation. The DCB test specimen was one inch wide and six inches long with no taper. The mode I fracture energy was calculated using the compliance method.

Results from short beam shear and flexure tests are given in Table I. Overall values are typical for carbon fiber/organic matrix composites. Flexure moduli are somewhat lower than expected based on the modulus of the carbon fiber used. These lower values are believed to arise from fiber misalignment incurred during the molding process.

TABLE I

Short Beam Shear and Flexure Properties of AS-4/LARC TM -TPI 1500 (high flow grade)/PAA Composites

Test Temperature, °C. (°F.)	SBS Strength, ksi	Flexural Strength, ksi	Flexural Modulus, Msi
Room Temperature	13.6	228	11.3
93 (200)	12.9	217	10.7
149 (300)	9.9	211	12.1
177 (350)	8.9	188	11.7

G_{IC} fracture toughness was measured to be 7.1 in-lb/in^2 which is well in the range of what is considered to be a tough composite material. Initiation and propagation values were identical and no fiber bridging was observed indicating that the specimen was uniform and well consolidated.

EXAMPLE II

Composites of LARC TM -TPI polyimide and Hercules AS-4 carbon fiber were prepared in the following manner. LARC TM -TPI 1500 pre-imidized powder (medium flow grad) was obtained from Mitsui Toatsu Chemicals. The asreceived powder contained particle agglomerations and was ground to a median particle diameter of 16 μm. LARC TM -TPI poly(amic acid) (PAA) powder was received as a coarse powder and was ground finer to reduce the time required to dissolve it.

To formulate the LARC TM -TPI slurry, a basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then. 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Finally 350.5 g of LARC TM -TPI 1500 pre-imidized powder was dispersed into the solution resulting in a stable slurry containing approximately 20% solids polymer with a 7.5:1 ratio of pre-imidized powder to PAA (based on the imide form of the PAA). Also, 4.85 g of p-PDA/PA flow enhancing dopant was added to improve the melt-flow of the polyimide. p-PDA/PA was prepared by reacting phthalic anhydride (PA) with p-phenylene diamine (p-PDA) at a 2:1 molar ratio in a solvent mixture of diglyme and 1-methyl-2-pyrrolidinone.

The polyimide slurry was deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow was pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup was controlled using a die of fixed gap at the dip tank exit. The fiber was taken up on a drum that had a diameter of 61 cm. The resulting prepreg had a fiber areal weight of approximately 140 g/m^2. The prepreg was air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites were formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings were carried out in a heated hydraulic press. Panels were fabricated at molding pressures of 1000 psi. A series of temperature ramps and holds was used to prevent the PAA molecular weight from increasing too rapidly and hindering melt flow. The heating ramps were fixed at 5.6° C./min. The isothermal holds were as follows: 260° C. for 75 minutes, 288° C. for 45 minutes, 302° C. for 90 minutes, and finally 371° C. for 60 minutes.

Panels were ultrasonically scanned at a sensitivity level sufficient to detect microvoids in standard epoxy/-graphite composites. All panels had C-scans showing complete consolidation over greater than 90% of their areas.

Results from short beam shear and flexure tests are given in Table II. Overall values are typical for carbon fiber/organic matrix composites. Flexure moduli are somewhat lower than expected based on the modulus of the carbon fiber used. These lower values are believed to arise from fiber misalignment incurred during the molding process.

TABLE II

Short Beam Shear and Flexure Properties of AS-4 LARC TM -TPI 1500 (medium flow grade)/PAA Composites

Test Temperature, °C (°F)	SBS Strength, ksi	Flexural Strength, ksi	Flexural Modulus, Msi
Room Temperature	13.2	229	12.9
93 (200)	11.9	228	12.5
149 (300)	9.8	200	13.1
177 (350)	8.5	175	11.4

G_{IC} fracture toughness was measured for two specimens. Values of 5.6 and 5.8 in-lb/in^2 were obtained which are well in the range of what is considered to be a tough composite material. Initiation and propagation values were identical and no fiber bridging was observed indicating that the composites were uniform and well consolidated.

EXAMPLE III

A Composite of LARC TM -TPI polyimide and Hercules AS-4 carbon fiber was prepared in the following manner. LARC TM -TPI 1500 pre-imidized powder (medium flow grade) was obtained from Mitsui Toatsu Chemicals. The asreceived powder contained particle agglomerations and was ground to a median particle diameter of 16 μm. LARC TM -TPI poly(amic acid) (PAA) powder was received as a coarse powder and was ground finer to reduce the time required to dissolve it.

To formulate the LARC TM -TPI slurry, a basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then, 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Finally 350.5 g of LARC TM -TPI 1500 pre-imidized powder was dispersed into the solution resulting in a stable slurry containing approximately 20% solids polymer with a 7.5:1 ratio of pre-imidized powder to PAA (based on the imide form of the PAA). Also, 4.85 g of p-PDA/PA flow enhancing dopant was added to improve the melt-flow of the polyimide. p-PDA/PA was prepared as in Example II.

The polyimide slurry was deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow was pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup was controlled using a die of fixed gap at the dip tank exit. The fiber was taken up on a drum that had a diameter of 61 cm. The resulting prepreg had a fiber areal weight of approximately 140 g/m^2. The prepreg was air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

A Unidirectional composite was formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings were carried out in a heated hydraulic press. Panels were fabricated at molding pressures of 300 psi. A series of temperature ramps and holds was used to prevent the PAA molecular weight from increasing too rapidly and hindering melt flow. The heating ramps were fixed at 5.6° C./min. The isothermal holds were as follows: 260° C. of 75 minutes, 288° C. for 45 minutes, 302° C. for 90 minutes, and finally 371° C. for 60 minutes.

The panel was ultrasonically scanned at a sensitivity level sufficient to detect microvoids in standard epoxy/-graphite composites. The panel had a C-scan showing complete consolidation over greater than 80% of its area.

EXAMPLE IV

A composite is prepared from a poly(arylene-ether) by the following method. A basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then, 49.5 g of PAA was added slowly with stirring in approximately

10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution has a viscosity of less than 300 cps. Next, a poly(arylene-ether) powder such as poly(aryl-ether-ether-ketone) is dispersed into the solution resulting in a stable slurry.

The slurry is deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow is pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup is controlled using a die of fixed gap at the dip tank exit. The fiber is taken up on a drum that has a diameter of 61 cm. The prepreg is air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites are formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings are carried out in a heated hydraulic press and panels are fabricated under pressure.

EXAMPLE V

A composite is prepared from a polysulfone by the following method. A basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then, 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Next, a polysulfone powder such as poly(phenylene-sulfide) is dispersed into the solution resulting in a stable slurry.

The slurry is deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow is pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup is controlled using a die of fixed gap at the dip tank exit. The fiber is taken up on a drum that has a diameter of 61 cm. The prepreg is air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites are formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings are carried out in a heated hydraulic press and panels are fabricated under pressure.

EXAMPLE VI

A composite is prepared from a polybenzimidazole by the following method. A basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then, 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Next, a polybenzimidazole powder is dispersed into the solution resulting in a stable slurry.

The slurry is deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow is pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup is controlled using a die of fixed gap at the dip tank exit. The fiber is taken up on a drum that has a diameter of 61 cm. The prepreg is air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites are formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings are carried out in a heated hydraulic press and panels are fabricated under pressure.

EXAMPLE VII

A composite is prepared from a liquid-crystalline polymer by the following method. A basic solution was first prepared by adding 11.8 g of a 30% aqueous ammonia (NH_3) solution to 1588.2 g of water. Then, 49.5 g of PAA was added slowly with stirring in approximately 10 g increments until all of the PAA was dissolved. A 3% solids PAA solution was obtained. The ratio of NH_3 to organic acid groups was 1.125:1 (a slight excess of base) in order to promote the dissolution of PAA. The solution had a viscosity of less than 300 cps. Next, a liquid-crystalline polymer powder such as polybenzoxazole is dispersed into the solution resulting in a stable slurry.

The slurry is deposited on un-sized 12k AS-4 carbon fiber using a standard drum winding technique. The carbon fiber tow is pulled through a dip tank containing a series of roller bars immersed in the slurry to enhance fiber spreading and wetting. Resin pickup is controlled using a die of fixed gap at the dip tank exit. The fiber is taken up on a drum that has a diameter of 61 cm. The prepreg is air-dried on the drum for several hours to remove a large portion of the water, then cut from the drum and dried in a forced-air oven at 204° C. (400° F.) for one hour to remove the remaining water and NH_3 from imidization.

Unidirectional composites are formed by stacking prepreg plies between Kapton® film coated with a release agent in a matched-metal mold. The moldings are carried out in a heated hydraulic press and panels are fabricated under pressure.

We claim:

1. An aqueous process for preparing a consolidated composite laminate comprising:

(a) preparing an aqueous poly(amic acid) surfactant solution comprised of poly(amic acid) powder and an aqueous ammonia solution;

(b) forming an aqueous slurry comprised of the poly(amic acid) surfactant solution and a polymeric powder;

(c) depositing the aqueous slurry on carbon fiber to form a prepreg;

(d) drying the prepreg;

(e) stacking the prepreg to form a composite laminate; and

(f) consolidating the composite laminate at pressures from about 300–1000 psi and heating at a temperature to imidize the poly(amic acid) and to impart melt flow in the polymeric powder.

2. The process of claim 1. wherein said poly(amic acid) surfactant solution is about 3% solids poly(amic acid).

3. The process of claim 1. wherein said aqueous slurry is about 5-20% solids polymeric powder.

4. The process of claim 1. wherein said polymeric powder is selected from the group consisting of: polyimide. poly(arylene-ether), polysulfone. polybenzimidazole. and liquid-crystalline polymers.

5. The process of claim 4. wherein said polymeric powder is a polyimide.

6. The process of claim 1. wherein said aqueous slurry is deposited on the carbon fiber by dipping.

7. The process of claim 1. wherein said prepreg is dried at room temperature.

8. The process of claim 1. wherein said prepreg is dried in a forced-air oven.

9. The process of claim 1. wherein said pressure is 1000 psi.

10. The process of claim 1. wherein said poly(amic acid) surfactant solution imidizes and forms a blend with the polymeric powder.

11. The process of claim 1. wherein said poly(amic acid) solution binds the polymeric powder to the carbon fiber.

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