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<p>(21) International Application Number: PCT/US98/07876 (22) International Filing Date: 17 April 1998 (17.04.98) (30) Priority Data: 08/844,481 18 April 1997 (18.04.97) US (71) Applicant: U.S. BORAX INC. [US/US]; 26877 Tourney Road, Valencia, CA 91355-1847 (US). (72) Inventor: SCHUBERT, David, M.; 11252 Nebraska Avenue, Los Angeles, CA 90025 (US). (74) Agent: THORNTON, James, R.; 26877 Tourney Road, Valencia, CA 91355-1847 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	

(54) Title: METHOD FOR PRODUCING CALCIUM BORATE

(57) Abstract

An improved method is provided for producing crystalline calcium hexaborate tetrahydrate, synthetic nobleite, by the reaction of boric acid and lime in an aqueous slurry. Reaction conditions include boric acid to water molar ratios of greater than 0.25:1, lime to boric acid molar ratios in the range of 0.05-0.15:1 and temperatures in the range of 60°-85 °C. A concentration of at least 25 % by weight undissolved solids is in the aqueous product slurry.

METHOD FOR PRODUCING CALCIUM BORATE

This invention relates to a method for the production of calcium borate and more particularly to an improved method for producing crystalline calcium hexaborate tetrahydrate, a synthetic form of the mineral nobleite, by the reaction of boric acid and lime in an aqueous slurry.

BACKGROUND OF THE INVENTION

Calcium borates have many industrial applications. They are used as a source of boron in fiberglass manufacture when the desired glass composition requires that sodium addition be limited, such as for textile fiberglass. They are also useful as fire retardant agents in such materials as plastics and rubber polymers, cellulose, resins and oils, etc. Further, they are useful in the manufacture of steel and ceramics.

Many different calcium borate compositions are known, both natural and synthetic; they are most commonly formed as hydrated compounds. Naturally occurring calcium borates which are commonly used commercially include colemanite, which has the chemical composition $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$, and ulexite, a mixed sodium-calcium borate of the composition $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$. Disadvantages of these naturally occurring calcium borate minerals include the presence of mineral impurities, the need for fine grinding when very fine particle sizes are needed, such as to achieve fine dispersions in polymeric resins for fire retardant applications, and in the case of ulexite, the presence of sodium and substantial water content. The borate contents of colemanite and ulexite are about 51% B_2O_3 and 43% B_2O_3 , respectively.

Known synthetic calcium borates include the tetrahydrate and hexahydrate forms of calcium metaborate, $\text{CaO}\cdot \text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ and $\text{CaO}\cdot \text{B}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, which contain about 35% and 30% B_2O_3 , respectively. Although these synthetic compositions have the potential of being of higher purity, since they lack the mineral impurities found in naturally occurring colemanite and ulexite, they are relatively low in borate content by comparison. Synthetic gowerite, consisting of calcium hexaborate pentahydrate ($\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$), contains

about 59% B₂O₃, which is substantially higher in borate content than the calcium metaborate compositions. However, gowerite tends to crystallize in a coarse, granular form, thus requiring grinding to achieve the fine particle sizes needed for many applications.

5 Calcium hexaborate tetrahydrate, which has the formula CaO·3B₂O₃·4H₂O, has the same ratio of boron to calcium as synthetic gowerite, but contains less water. At 62% B₂O₃ it has a higher borate content than gowerite, the calcium metaborates and the minerals colemanite and ulexite. It is known to occur in nature as the mineral nobleite, although it is not found in commercially exploitable quantities.

10

Various methods for producing synthetic forms of the minerals nobleite and gowerite are known. For example synthetic nobleite can be produced by the hydrothermal treatment of meyerhofferite (2CaO·3B₂O₃·7H₂O) in boric acid solution for 8 days at 85°C. See U.S. Patent No. 3,337,292.

15

Ditte, Acad. Sci. Paris Coptes rendus, 77, 783-785 (1873), described the formation of lime borates by reaction of Iceland spar (calcite) with a saturated boric acid solution. The resultant salt was described as small needles of "a hydrated limeborate" which contains "3BoO², CaO,HO)(BoO²,3HO)." Subsequently, Erd, McAllister and Vlisidis, American
20 Mineralogist, 46, 560-571 (1961), suggested the Ditte product was nobleite. Erd et al. also synthesized nobleite by stirring CaO and boric acid in water for 30 hours at 48°C, and then holding the product at 68°C for 10 days.

Kemp, The Chemistry of Borates, Part I, page 70 (1956), reported that an aqueous
25 solution of boric acid kept at 40°C for 3 weeks deposits a mixture of CaO·3B₂O₃·4H₂O and 2CaO·3B₂O₃·9H₂O. Kemp also reported that CaO·3B₂O₃·8H₂O decomposes to form CaO·3B₂O₃·4H₂O. According to Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume V, Part A: Boron-Oxygen Compounds, pages 550-551 (1980), CaO·3B₂O₃·4H₂O occurs as a solid phase in the systems: Na₂O-
30 CaO-B₂O₃-H₂O and CaO-NaCl-B₂O₃-H₂O at 25°C and pH 5.5-6.5. Hydrothermal treatment of meyerhofferite in boric acid solution at 85-250°C produced crystals of both the tetrahydrate and pentahydrate together with ginorite (2CaO·7B₂O₃·8H₂O).

Mellor further reported that nobleite is a stable phase in the CaO-B₂O₃-H₂O system at 25°C and at 45°C and is also formed from an aqueous mixture of lime (CaO) and boric acid at 60°C. Also, Mellor reports on page 551 that CaO·3B₂O₃·5H₂O (gowerite) is
5 formed from lime and boric acid in aqueous media at 100°C.

Lehmann et al, Zeitschrift für Anorganische und Allgemeine Chemie, Volume 346, pages 12-20, (1966), teach that the formation of gowerite from CaO, H₃BO₃ and water is favored by a relatively high temperature (100°C), and higher CaO concentration, whereas
10 nobleite formation is predominantly formed in more dilute solutions with lower CaO content and at a lower temperature (60°C).

The present applicant has found that a novel crystalline calcium hexaborate tetrahydrate composition having a distinctive crystal habit can be produced by reaction of
15 lime with boric acid in an aqueous slurry at a temperature in the range of from about 60° to 85°C, provided that the final concentration of undissolved solids in the aqueous product is at a high level and the molar ratio of lime to boric acid (CaO:H₃BO₃) added is within specific limits. The resultant crystalline tetrahydrate product will generally have a desirable crystalline habit consisting of thin, intergrown platelets arranged in nearly spherical radial
20 clusters.

SUMMARY OF THE INVENTION

25 This invention provides an improved method for producing a crystalline calcium hexaborate tetrahydrate, by the reaction of boric acid and lime in an aqueous slurry at a temperature in the range of from about 60° to 85°C, wherein the molar ratio of boric acid to water (H₃BO₃:H₂O) is greater than about 0.25:1 and the molar ratio of lime to boric acid (CaO:H₃BO₃) is in the range of from about 0.05 to about 0.15:1, and the reactants are
30 present in a concentration sufficient to provide at least 25% by weight undissolved solids in the aqueous product slurry. The method of this invention results in a rapid reaction rate, high product yield and favorable product characteristics such as fine particle size distribution, with good flow and bulk handling properties. Further, there is provided a

novel crystalline calcium hexaborate tetrahydrate composition having a distinctive crystal habit.

DETAILED DESCRIPTION OF THE INVENTION

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The method of this invention comprises reacting high concentrations of boric acid and lime in water at elevated temperatures, in the range of from about 60° to about 85°C, to form crystalline calcium hexaborate tetrahydrate. The preferred reaction temperatures are at the elevated temperatures, and preferably in the range of from about 70° to about 85°C. A high concentration of undissolved solids in the reaction mixture is required, such as would provide at least 25% by weight undissolved solids in the final product slurry and preferably at least 30% by weight.

15

The concentration of the reactants is important to the production of calcium hexaborate tetrahydrate according to the process of this invention. In particular, a high ratio of boric acid to water in the reaction mixture will produce nobleite rather than gowerite at elevated temperature conditions of this invention. Boric acid, which is highly soluble in water at high temperatures, should be added in quantities which are substantially greater than the solubility limit, in order to produce nobleite at these temperatures. The molar ratio of boric acid to water ($H_3BO_3:H_2O$) in the starting mixture should be greater than about 0.25:1, such as in the range of from about 0.25 to 0.5:1 and preferably in the range of from about 0.3 to 0.45:1. This is substantially higher than the solubility limit of boric acid at temperatures of 60° to 85°C which ranges from about 0.04 to about 0.08 moles of H_3BO_3 per mole of water.

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The molar ratio of lime to boric acid ($CaO:H_3BO_3$) in the starting mixture is in the range of from about 0.05 to 0.15:1, and preferably about 0.1 to 0.14:1. As used herein, lime includes calcium oxide such as burnt lime and quick lime, calcium hydroxide such as hydrated lime, slaked lime and lime hydrate, and calcium carbonate, including calcite and limestone.

30

The method of this invention may be used in producing calcium hexaborate tetrahydrate in a batch, continuous or semi-continuous process. In a batch process, the boric acid and lime may be combined in water and heated at the required temperature range to initiate the reaction. Alternatively, a mother liquor recycled from previous runs or
5 freshly prepared mother liquor may be used as the reaction media. In a continuous or semi-continuous process, the desired product is continuously removed from the reaction vessel and the remaining mother liquor is recycled by adding additional boric acid and lime and heating the reactants at the reaction temperatures.

10 Generally the reaction is essentially complete within one hour, although small improvements in the product B_2O_3 analysis may be attained by heating the reaction mixture for up to about 4 hours. When calcium oxide or calcium hydroxide are used as reactants, the reaction occurs as a noticeable exotherm within about 15 to 25 minutes, during which time the majority of the starting materials are converted to the desired product.

15 Preferably, the reaction mixture is agitated, such as by stirring, during the reaction period. After the reaction is completed, the nobleite product is separated from the hot mother liquor such as by filtration or centrifugation or other suitable mean of solid-liquid separation. The wet solids may be washed, such as with water, to remove any entrained
20 mother liquor, and subsequently dried to provide a crystalline calcium hexaborate tetrahydrate.

If a product with higher B_2O_3 content is desired, the calcium borate tetrahydrate can be dehydrated by heating at a temperature of at least about $325^\circ C$, preferably in the range
25 of about $450^\circ C$ to about $600^\circ C$ to produce a novel amorphous, anhydrous calcium hexaborate, $CaO \cdot 3B_2O_3$, which contains about 79% B_2O_3 .

30 Particle size analysis of the crystalline product of this invention indicates a relatively small mean particle size distribution, typically of about 90% less than 75 micrometers in diameter. This small mean particle diameter is advantageous for many applications where a fine dispersion of the solids is required, such as for fire retardant applications in polymeric resins. Yet it is easy to filter, facilitating the separation of the solid product from the

mother liquor, which can then be recycled back into the process. Further, the spherical shape of the crystal habit results in excellent handling and flow properties of the dried solids despite the extremely fine particle size distribution. It was also found that the crystalline product does not have a significant tendency toward caking.

5

The product dehydrates in three distinct stages, losing water at about 91°, 177° and 312°C. It was found to melt at a temperature of about 927°C. The anhydrous calcium borate product produced by dehydration of the product is less hygroscopic than most dehydrated metal borate compounds.

10

EXAMPLE 1

15 A 12-L flask was fitted with a reflux condenser, mechanical stirrer, and temperature controller. A mother liquor was prepared by charging the flask with 5 kilograms of deionized water, 1448 grams (23.42 moles) boric acid, and 31.7 grams (0.43 mole) calcium hydroxide. The mixture was heated to 80°C, and 1876 grams (30.34 moles) of boric acid, 417 grams (5.63 moles) of calcium hydroxide and 3 grams of synthetic nobleite seed were
20 added. A second addition of 1876 grams of boric acid and 417 grams of calcium hydroxide was made to give a reaction slurry with a boric acid to water ($H_3BO_3:H_2O$) molar ratio of 0.30:1 and a lime to boric acid ($CaO:H_3BO_3$) molar ratio of 0.14:1. The amounts of reactants were calculated to yield a final product slurry containing about 36% by weight undissolved solids, assuming complete conversion of lime to a solid nobleite product.
25 Reactant addition resulted in a temperature drop to 72°C, but continued heating led to a return to 80°C within 9 minutes. After 20-25 minutes from reactant addition an exotherm occurred giving a temperature rise to 86°C. The mixture gradually returned to the control temperature of 80°C where it was maintained with stirring. A chemical analysis of the solid phase yielded 61.2% B_2O_3 after a total of 165 minutes, indicating that the reaction was
30 essentially complete. The reaction was allowed to stir overnight at 80°C. After 21 hours the product slurry was filtered, and the filtered solid was washed with water and air dried, resulting in a free flowing white powder. The crystalline product was determined to be nobleite by X-ray diffraction analysis. Chemical analysis indicated that the final product

contained 62.3% B₂O₃. The product had a particle size distribution of 99% by weight passing a 100 mesh (150 micrometer) test sieve, 97% by weight passing a 200 mesh (75 micrometer) test sieve and 94% by weight passing a 325 mesh (45 micrometer) test sieve. The material appeared to have good flow properties, but tended to fluidize easily leading to bimodal flow behavior.

EXAMPLE 2

10 Boric acid (603.4 grams) and 13.2 grams of calcium hydroxide (Ca(OH)₂) were combined in 2,083.5 grams of deionized water in a stirred flask to make up a batch of synthetic mother liquor. This mixture was stirred and heated to 60°C and two batches, each of 781.7 grams of boric acid and 173.8 grams of calcium hydroxide, were added to give a reaction slurry with a lime to boric acid (CaO:H₃BO₃) molar ratio of 0.14:1 and a boric acid to water (H₃BO₃:H₂O) molar ratio of 0.30:1, which was calculated to yield a final product slurry containing about 36% by weight undissolved nobleite solids. There was a slight drop in temperature after the addition of each batch of reactants.

15 Approximately 3.0 grams of previously prepared synthetic nobleite was added as seed material after the final addition of boric acid and lime to promote crystallization of the nobleite product. A temperature increase to 63.1°C was observed about 25 minutes after the addition of nobleite seed. The reaction mixture was stirred continuously with the temperature maintained at 60°C for a period of 20 hours from the start of the test. At the conclusion of the 20-hour period the reaction slurry was filtered and the filter cake was washed with 1500 grams of deionized water to remove adhering liquor and then dried at about 60°C for four days. The resultant crystalline product, which contained about 63.8% B₂O₃ and 16.1% CaO, was determined to be nobleite by X-ray diffraction analysis.

EXAMPLE 3

30 In 2,000 grams of water was combined 579.2 grams of boric acid and 17.1 grams of calcium carbonate (Atomite[®] CaCO₃ from ECC America Inc., mean particle size 3 μm) and the resultant mixture heated to 80°C. A mixture of 835.6g boric acid and 225.3g calcium carbonate was slowly added, causing the slurry to foam due to the release of carbon

dioxide gas and to drop in temperature to 70°C. After the foaming had subsided and the temperature returned to 80°C a second mixture of 835.6g boric acid and 225.3g calcium carbonate was added. The slurry was again reheated to and maintained at 80°C. The molar ratios of boric acid:water and lime:boric acid were 0.33:1 and 0.13:1, respectively.

5 The reaction mixture was calculated to yield a final product slurry containing about 35% by weight undissolved nobleite solids. The reaction mixture was sampled after three hours and the entire batch was filtered and washed with deionized water after five hours, then dried at 60°C for several days. The product was analyzed by titration and found to contain 63.4% by weight B₂O₃ after five hours of reaction time. The final product was determined by X-
10 ray diffraction to be nobleite.

EXAMPLE 4

15 The same procedure as example 3 was followed except that the reaction was carried out at 60°C instead of 80° and the batch size was reduced by 25% to accommodate the foaming caused by the evolution of carbon dioxide gas. As in example 3, the molar ratios of boric acid:water and lime:boric acid were 0.31:1 and 0.14:1, respectively, to yield a calculated final product slurry containing about 35% by weight undissolved nobleite solids.

20 The reaction mixture became very thick after three hours. It was allowed to stir overnight and became so thick during this time that it appeared to be stirring only in the center of the reaction mixture. Two liters of deionized water at 60°C were added in order to thin the slurry before attempting to filter the mixture. However, the product was very difficult to filter and appeared to contain very fine particulate solids. The solid product was analyzed
25 by X-ray diffraction and determined to be nobleite. Evaluation of the product by scanning electron microscopy indicated that the nobleite had formed as hexagonal platelets, however the unique morphology, wherein the platelets form as spherical radial clusters at higher temperature, was largely absent as many of the platelets were unattached. The product was analyzed by titration and found to contain about 62.3% by weight B₂O₃.

30

EXAMPLES 5-6

Reactions were carried out at 75°C and at lower boric acid:water ratios (and therefore lower final solids concentrations) using calcium hydroxide as the source of lime. In example 5, boric acid (1,448 grams) and 31.7 grams of calcium hydroxide were combined with 5 liters of deionized water and heated to 75°C. An additional 1,506 grams of boric acid and 300.7 grams of calcium hydroxide were added. The molar ratios of boric acid:water and lime:boric acid were 0.17:1 and 0.09:1, respectively. The mixture was calculated to yield a final product slurry containing about 18% by weight undissolved solids, assuming complete conversion of lime to a solid nobleite product. After 45 minutes a crop of particles was observed. After three hours the reaction mixture was sampled and then diluted to 50% with warm water and filtered. The filter cake was washed with about 3 liters of deionized water to remove adhering liquor. The solid product was analyzed by titration and found to contain 61.8% by weight B₂O₃. The product was determined to consist of nobleite with an estimated 7% gowerite based on X-ray diffraction analysis.

Example 6 was similar to example 5, except it was run at a much lower boric acid concentration. In example 6, boric acid (1321 grams) and 20 grams of calcium hydroxide were combined with 6,419 grams of deionized water and heated to 75°C. An additional 100 grams of boric acid and 140 grams of calcium hydroxide were added. The molar ratios of boric acid:water and lime:boric acid were 0.06:1 and 0.09:1, respectively. The mixture was calculated to yield a final product slurry containing about 9% by weight undissolved solids, assuming complete conversion of lime to a solid nobleite product. After three hours the reaction mixture was sampled and filtered. The solid product was found to contain a poorly crystallized mixture of nobleite and gowerite. The product was analyzed by titration and found to contain only 46.5% by weight B₂O₃.

Various changes and modifications of the invention can be made and, to the extent that such variations incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. The method of producing crystalline calcium hexaborate tetrahydrate which comprises reacting boric acid and lime in an aqueous slurry, at a temperature in the range of from about 60° to about 85°C, wherein the molar ratio of boric acid to water is greater than about 0.25:1, and the molar ratio of lime to boric acid is in the range of about 0.05 to about 0.15:1, wherein said reactants are present in a concentration sufficient to provide at least 25% by weight undissolved solids in the aqueous product slurry, and separating said crystalline calcium hexaborate tetrahydrate from said aqueous product slurry.
2. The method according to claim 1, wherein said molar ratio of boric acid to water is in the range of from about 0.3 to about 0.45:1.
3. The method according to claim 1, wherein said molar ratio of lime to boric acid is in the range of from about 0.1 to about 0.14:1.
4. The method according to claim 1, wherein said temperature is in the range of from about 70° to about 85°C.
5. The method according to claim 1, wherein said lime is calcium carbonate.
6. The method according to claim 1, wherein said lime is hydrated lime.
7. The method according to claim 1, wherein the concentration of undissolved solids in said aqueous product slurry is at least about 30% by weight.
8. The method of producing crystalline calcium hexaborate tetrahydrate which comprises reacting boric acid and lime in an aqueous slurry, at a temperature in the range of from about 70° to about 85°C, wherein the molar ratio of boric acid to water is in the range of from about 0.3 to about 0.45:1, the molar ratio of lime to boric acid is in the range of from about 0.1 to about 0.14:1, and the concentration of reactants provides at least 30% by

weight undissolved solids in the aqueous product slurry, and separating said crystalline calcium hexaborate tetrahydrate from said slurry.

5 9. Crystalline calcium hexaborate tetrahydrate consisting of thin, intergrown platelets, arranged in nearly spherical radial clusters.

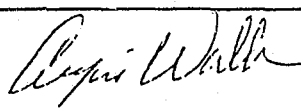
10 10. The method of dehydrating the crystalline calcium hexaborate tetrahydrate composition of claim 9 wherein said composition is heated at a temperature above about 325°C.

11. The method according to claim 10 wherein said temperature is in the range of from about 450°C to about 600°C.

15 12. An amorphous calcium hexaborate composition produced according to the process of claim 10.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/07876

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(6) : C01B 35/12 US CL : 423/279,280 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 423/279,280		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) none		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,683,126 A (INOUE ET AL) 28 July 1987 (28.07.87), see column 4, lines 51-59; column 5, lines 42-59; column 9, lines 25-38.	1-9, 12
A	US 4,179,493 A (SADAN) 18 December 1979 (18.12.79), see column 1, lines 4-36.	9, 12
A	SU 1,321,678 A1 (ALEKHIN ET AL) 07 July 1987 (07.07.87), see entire document.	1-9, 12
A	SU 1,754,656 A1 (ALEKSHEV ET AL) 15 August 1992 (15.08.92) see entire document.	1-9, 12
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 01 JULY 1998	Date of mailing of the international search report 20 JUL 1998	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Wayne Langel  Telephone No. (703) 308-0661	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/07876**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 10-11
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

They recite a method but depend from claim 9, which is a composition.

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.