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(54) Title: CERAMIC SHELL MOLD (57) Abstract Method for making a novel shell mold for use in directional solidification and for casting alloys containing reacting components, wherein a binder comprising a non-fibrous aqueous acidic dispersion of alumina monohydrate and being essentially free of silica, is employed. The resultant shell mold is particularly suitable for the casting of nickel and cobalt based alloys containing relatively reactive constituents such as zirconium, aluminum and titanium.		

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Ceramic Shell Mold

Technical Field

This invention relates to the manufacture of refractory coatings and in particular, shell molds for use in directional solidification and for casting alloys
5 containing reactive components.

Background Art

The predominant process for making small and intricate castings such as turbine blades, vanes, nozzles and many other parts is the ceramic shell mold process.
10 A group of expendable patterns of parts to be cast are made, for example, in wax, and set up into a cluster. This cluster is then dipped into a ceramic slurry, removed and coarse refractory is sprinkled on the wet slurry coating and allowed to harden or "set".
15 This process is repeated several times until a sufficient thickness of ceramic is built up onto the wax pattern. Drying or chemical setting can be carried out on each layer. After the final thickness is reached, the entire assembly is "set" or dried.
20 The wax is then removed by one of several acceptable techniques, such as in a steam autoclave or by actually firing the mold to melt out the wax. The mold is then preheated to an appropriate temperature and the metal is poured into the resulting mold.



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Instead of wax, the expendable pattern may be formed of polystyrene, plastic modified wax etc.

The usual refractories used in this system are fused silica, crystalline silica, aluminosilicates, zircon, and alumina.

Heretofore, bonding of these refractory particles has been mostly carried out by an alcoholic solution of hydrolyzed ethyl silicate or a colloidal dispersion of silica in water. Upon drying of the shell molds, the silica serves as a bond for the refractory particles. Typical ceramic shell mold processes are given in the following U.S. patents: 3,165,799, 3,933,190, 3,005,244 and 3,955,616.

The deficiencies of silica-bonded shell molds are particularly apparent in the directional solidification technique of casting:

Such technique has been developed for producing castings having directionally solidified grains, which is particularly applicable to the manufacture of turbine blades wherein the blade has longitudinal grains, whereby the high temperature properties are improved as a result of the grain structure. One of the techniques used in producing such structures is described in the Ver Snyder U.S. Patent 3,260,505. Because of the long slow cooling rates, the alloys poured, which many times contain some relatively reactive constituents, are left exposed to the hot mold for long periods of time. With silica bonds, such exposure causes a



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reaction with the bond by some alloys and produces a casting having a relatively poor surface and relatively poor high temperature properties.

Further when an alloy is poured into a ceramic mold, which is usually around 1800°F in normal casting operations, the alloy almost immediately solidifies, or else it solidifies immediately adjacent to the mold, because of the wide discrepancy in temperature. This solidification means a crystal formation and accordingly the casting comes out as an equiaxed grain casting. In directional solidification, the technique is to start the crystal growth from the base of a blade; for example, to grow vertically or longitudinally to form a long crystal in the direction of the blade length for best results. The less the discrepancy between the metal temperature and the mold temperature, the greater are the probabilities of being able to do this. Ideally, a mold should be at at least the solidification point of the alloy or above, so that when the metal is poured in, it will not immediately solidify adjacent to the mold surface, but then the cooling can be controlled from any direction that it is desired to do so. Therefore, by having molds that can withstand higher than normal casting temperatures, more control on grain structure can be obtained. The general maximum service temperature for conventional molds is now approximately 2500°C. Anything above this leads to softening of the silica bonds now



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normally used and aggravates reactivity problems.

One attempt to overcome the reactivity problems with silica molds is described in U.S. Patent 3,933,190 relating to the use of aluminum polyoxychloride
5 binder with an alumina refractory to form the mold. However, this type of binder has very poor green and elevated temperature strengths, thereby making it difficult to dewax the mold without cracking and destroying the mold surface. Likewise the aluminum
10 polyoxychloride is soluble in steam, which does not permit the mold to be autoclave dewaxed.

Some observers have shown that alumina is relatively inert compared to silica with most nickel and cobalt based alloys containing minor quantities of reactive
15 compounds and thus a satisfactory all-alumina shell is highly desirable.

A satisfactory all alumina shell mold is described in Serial No. 889,142 of the present inventor, filed March 20, 1978, however, it employs a fibrous type
20 colloidal alumina which is a rather expensive component.

In view of the foregoing, an objective herein is to provide an improved high temperature refractory coating.

Another object is to provide an improved high temperature shell mold.

25 Another object is to provide a relatively inexpensive, essentially all-alumina final shell mold for use in producing directionally solidified castings.

Yet another object of this invention is to



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provide a non-reactive mold surface for alloys containing reactive components.

Disclosure of Invention

These and other objects are realized by the present invention wherein the binder for making the shell mold comprises a non-fibrous, aqueous, acidic dispersion of alumina monohydrate, the binder being essentially free of silica.

By use of the above binder, the resulting mold exhibits excellent green strength which facilitates dewaxing in an autoclave or by other means and yet is significantly less expensive than the fibrous alumina shell mold of Serial No. 889,142.

The mold of the present invention also retains sufficient strength during the dewaxing operation to prevent cracking of the mold and has sufficient strength to permit preheating temperatures up to about 3100°F, e.g. 2750 to 3100°F.

Further, by virtue of the fact that an all-alumina system is provided, alloys containing reactive components such as nickel and cobalt-based alloys containing one or more of hafnium, zirconium, tungsten, aluminum, titanium, niobium, molybdenum, carbon, silicon, manganese or yttrium, can be poured without adverse effects due to their reactivity.



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Detailed Description

The basic method for making the shell mold comprises making an expendable pattern of a part to be cast, dipping the expendable pattern into a slurry of a ceramic powder and a binder to form a moist coating on said wax pattern, sprinkling a coarse refractory powder on said moist coating, drying said moist coating, and repeating dipping, sprinkling and drying, whereby said shell mold is built up to a desired thickness.

The binder of the present invention employs an aqueous acidic dispersion of alumina monohydrate in water. The alumina has an essentially spheroidal particle, i.e. it is non-fibrous and has a boehmite structure primarily. Needless to say, the binder should be essentially free of silica to avoid the above-discussed reactivity problems.

Typical commercially available alpha-alumina monohydrates are that produced under the Tradename "Dispural" obtained from Philadelphia Quartz and "Catapal" obtained from Conoco. The following tabulations are typical data on the characteristics of these two products:



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	Property	<u>Dispural</u>	<u>Catapal</u>
	Alpha-alumina monohydrate	90%	
	Water	9%	
	Carbon as primary alcohol	.5%	.36
5	SiO ₂	.008	.088
	Al ₂ O ₃ content		74.2
	Total ignition loss		25.8
	Surface area (BET)	320 sq/meters/ gm	250 sq. meters/gm
10	Particle size by sieving		
	less than 45 microns	85%	48%
	Greater than 90 microns		9%

Some of these materials are obtained from Ziegler reactions such as the use of triethyl aluminum to produce high-molecular-weight trialkyl aluminums which are oxidized to yield aluminum alkoxides. These are then hydrolyzed with water to yield alumina monohydrate. Varying trace amounts of acid, such as sulfuric, may also be present.

The above alumina dispersions exhibit a tendency to gel outside of their normal pH range. Therefore it is essential to maintain the pH within precisely controlled limits, i.e. 2.7 to 5.4 and preferably 3.6 to 4.4

Failure to control the pH within the above range creates serious problems if the alumina is to be used as a binder for shell molds, because the refractories used contain small amounts of impurities such as alkalis,



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and this is particularly true with the commercial tabular alumina. The acidity of the alumina dispersion acts to neutralize this alkali in the fine flours used and therefore the pH of the dispersion remains in the stable range.

A variety of acids can be used in rendering the dispersion sufficiently acidic.

The preferred acids used are mineral acids, such as hydrochloric, sulfuric, and nitric but strong organic acids such as monochloroacetic acid can also be used.

A typical colloidal alumina sol that is relatively stable has been described in U.S. Patent 3,935,023. Previous work with this binder, when mixed with tabular alumina, produced relatively unstable slurries which could be prepared and could be applied as coatings, but would eventually gel. These slurries would generally become unstable when the weight ratio of alumina refractory to binder was increased beyond 2. The slurries would become thicker and progressively more thixotropic and would eventually become like a gel upon increasing the refractory to binder ratio from 2 to 3.75.

This invention thus provides a means for producing slurries that are stable enough from a practical standpoint to prepare shell molds of excellent quality.

If the alumina monohydrate already contains adequate acidic material, it may be possible to disperse it in plain water and it can be stable enough to



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produce an adequate slurry with sufficient shelf life.
The slurry can further be modified with acid if needed.

The drying and heating of the dispersion changes
it from alpha-alumina monohydrate to alpha-alumina and
5 then to gamma-alumina.

A variety of refractories can be used with the
binder of this invention, depending upon the particular
application.

Thus, for example, useful refractories include
10 on or more of quartz, fused silica, monoclinic zirconia,
stabilized electrically fused zirconia, mullite, alumino-
silicates, calcined alumina, fused alumina, ceria or
yttria.

Certain refractories, such as fused silica, do
15 not require the use of as much acid as other refractories.

In the case of directionally solidified castings,
alumina or a non-reactive refractory is best used.
Typical examples of a suitable alumina refractory is
fused alumina (Norton Grade 38), or tabular alumina
20 (Alcoa Grade T-61). Stabilized zirconia having a very
high softening temperature may also be used for high
temperature mold structures. Yttria, also having a
very low reactivity with reactive metals, may be
desirable for mold surfaces bonded with the alumina.
25 sol.

The number of alumina sol bonded coats may also
vary depending upon the needs of the particular
application.



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Ammonia treatments may or may not be used with this sol system for hardening. It is generally not necessary but can be used if desired. In this regard, the alumina sol treatment with ammonia vapors after each coat acts to further insolubilize the alumina dispersion. Exposure to ammonia vapors causes the dispersion to increase in pH, thereby bringing it out of the stable range and causes a preliminary set. It should be mentioned also that ammonia setting of the complete shell after dipping causes the entire shell to set and become water resistant. Prior to that, it is less water resistant than without ammonia.

For some applications, it may be desirable to apply only one or two coats of refractory bonded with alumina sol, and then back up the remaining coats with either a solid mold structure or additional shell structure containing a different bond, such as colloidal silica or hydrolyzed ethyl silicate.

For some of the more reactive alloys, all that is needed is for the casting mold surface to be free from reactive materials and therefore a single coating of an alumina sol-bonded alumina, ceria, yttria, or zirconia refractory mold, is thought to be adequate for most of the reactive alloys. This coating can then be backed up with either a solid mold structure or by another type of shell mold structure including those made with a different type of binder.



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In effect, as long as there is a totally non-reactive surface, i.e. by utilization of the present invention, it can be backed up with any other kind of a mold system that will withstand the casting conditions and alloys containing reactive metals.

Various aspects of the present invention will now be illustrated with reference to the following Examples which are not to be taken as limitative.

Example 1

In this Example and those following there is employed a slurry utilizing a sol of the type described in the above U.S. Patent No. 3,935,023.

A dispersion of Dispural was prepared according to the teachings of U.S. Patent No. 3,935,023 with 25% solids and having a density of 60°F of 1.19. This sol serves as the basis of the binder in slurries 1, 2, 3 and 4, as described in Table I.



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Table I

Slurry Number	Binder % Al_2O_3	Type Refractory	grams wt. Ref- ractory	cc. Volume Binder	Drops con. HCl	Drops Wetting Agent Sterox NJ*
1	20	Calcined Al_2O_3 A-17**	2200	600	100	10
2	20	zircon flour	1925	525	70	5
3	20	Calcined Al_2O_3 A-17**	1050	255	40	
4	20	Fused Silica Flour	1200	540	10	

These slurries were prepared to a viscosity of about 30 seconds measured by the #4 Zahn cup. The viscosity should be between 33 and 35 seconds. The first dip was applied to a test pattern composed of a rectangular sheet of wax. Immediately after dipping, a coarse fused alumina of a nominal 70 grain size was sprinkled over the wet pattern. This was then allowed to dry. The slurry in the meantime was reduced in viscosity by adding more of the alumina binder

*Available from Monsanto Corporation.

**Available from Alcoa Corporation.



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solution to a viscosity of about 15 seconds by #4 Zahn cup. At the end of the indicated drying time the pattern was redipped and sprinkled with the appropriate stucco grains. See Table II.



Table II

Stucco System Coatings

Slurry Number	1	2	3	4	5	6	7
1	70 grain Alundum	70 grain Alundum	-28 + Tabular Alumina	48 mesh Alumina	-14 + 28 mesh Tabular Alumina	-14 + 28 mesh Alumina	none
2	"	"	"	"	"	"	"
3	"	"	"	"	"	"	"
4	← approx. 70 grain Alundum →	← approx. -50 + 100 mesh Alundum →	← -28 + 100 mesh Tabular Alumina →	← 48 mesh Alumina →	← -14 + 28 mesh Tabular Alumina →	← -14 + 28 mesh Alumina →	← none →

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It was dried and this process continued until the seventh coat was applied, which did not receive a coarse refractory stucco. The final dipped pattern was then allowed to thoroughly dry at room temperature. Then,
5 for melting out the wax, a low temperature oven at about 110°C was employed.

The dipping times are summarized in Table III.



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Table III
Dipping Times

Slurry Number	1	2	3	4	5	6	7
1	1st day	2nd day	2nd day	3rd day	3rd day	3rd day	5th day
2	"	3rd day	3rd day	4th day	4th day	5th day	"
3	"	"	"	"	"	"	"
4	"	"	"	"	"	"	"

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The flat shell specimens on each side of the wax sheet were then cut into test specimens by means of a diamond saw to about 1" width by 2 1/2" length. These were tested on a transverse loading machine for breaking strength. Several specimens were broken to give an average value for room temperature modulus at rupture. Additional specimens were then fired to varying temperatures in a high temperature furnace according to a fairly rapid cycle within three hours, soaked at the maximum temperature for one hour, and then cooled in the furnace to room temperature. The specimens were then tested at room temperature for breaking strength. Values for each shell system are reported in Table IV.

Table IV

Modulus at Rupture*
lbs./sq.in

Slurry Number	Non-fired	Fired			
		1200°F	1800°F	2000°F	2500°F
1	1041		772		2457
2	1049	978	1153	1365	3203
3	1100	789	1286	1438	3155
4	918	439	349	350	968

*Fired to indicated temperature and cooled to room temperature and tested.



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The basic principle of obtaining a satisfactory slurry with a ratio of refractory to binder liquid of higher than 2 to 1 is to carefully and methodically add acid to the slurry.

5 Many times this can be done initially to a binder before adding refractory, but other times alternating acid and refractory additions is necessary. This appears to be related particularly to alumina refractory and one having considerable fines. By careful additions
10 of acid with suitable stirring a slurry can be prepared of a satisfactory viscosity without gelling and having a ratio of refractory to binder of more than 2 to 1.

Example 2

15 Two samples of a relatively acidic Dispural A and B (boehmite powders) were also used in preparing a sol. In view of their acidic nature, which probably was due to retained acid when it was removed from the original chemical reaction, they were used as binders. These were added to water and slurried along with the
20 refractory to prepare slurries 5 and 6. The following Table V gives the slurry composition.

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Table VSlurry Compositions

	<u>Slurry Number</u>	<u>Type Binder</u>	<u>Type Refractory</u>	<u>wt. grams Refractory</u>	<u>Weight Dispural</u>
5	5	Dispural A	A-17 Calcined Al_2O_3	1300	75
10	6	Dispural B	A-17 Calcined Al_2O_3	1300	75

The stucco coatings are described in the following
Table VI.



Table VI
Stucco System Coatings

Slurry Number	1	2	3	4	5	6	7
5	% M. Alundum	%M. Alundum	-28 + 48 Tabular	mesh Alumina	-14 + 28 Tabular	mesh Al ₂ O ₃	None
6	"	"	"	"	"	"	"

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These slurries were prepared in the same fashion as Example 1 and the modulus at rupture values is set forth in Table VII.

Table VII

Modulus at Rupture*
lbs./sq.in

Slurry Number	Non-fired	Fired			
		1200°F	1800°F	2000°F	2500°F
5	880	813	1076	1171	2296
6	630	399	415	519	554

*Fired to the indicated temperature and cooled to room temperature and tested.

The following Tables VIII and IX disclose analytical information relative to Dispural A and B.



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Table VIIIPhysical-Chemical Data of Selected Aluminas

		<u>Dispural A</u>	<u>Dispural B</u>
	Loss on drying, wt%	13.77	13.62
5	Al ₂ O ₃ , wt. %	68.69	69.09
	SiO ₂ , wt. %	0.015	0.028
	Fe ₂ O ₃ , wt. %	<0.01	<0.01
	Na ₂ O, wt. %	<0.01	<0.01
	Carbon, wt. %	0.13	0.15
10	TiO ₂ , wt. %	0.116	0.116
	Particle size, μ	1.3	1.7
	Surface area, m ² /g	213	207

Table IX

15 % Cl as HCl in Aqueous Dispersions of Dispural
 A and B

	<u>10% Solids</u>	<u>25% Solids</u>	<u>27% Solids</u>
Dispural A	0.008	0.017	0.019
Dispural B	0.287	0.718*	0

20 *Normalized to 25% analysis of 10% solids
 sample. At this level, gelling is avoided.

Industrial Applicability

It is contemplated that the instant binder and
 refractory material bound thereby find a wide variety
 of applications other than in shell molds, for example,
 25 other types of molds and equipment which require



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durability at elevated temperature, especially where contact with reactive molten metal, e.g. at temperatures between 2000 to 3100°F is involved.



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CLAIMS:

1. In a method for making a shell mold which comprises:

a. making an expendable pattern of a part to
5 be cast,

b. dipping the expendable pattern into a slurry of a refractory material and a binder to form a moist coating on said pattern,

c. sprinkling a coarse refractory powder on
10 said moist coating,

d. drying said moist coating,
and

e. repeating steps b, c and d, whereby said shell mold is built up to a desired thickness,
15 the improvement wherein said binder comprises an aqueous, acidic, dispersion of an essentially non-fibrous alumina monohydrate, said binder being essentially free of silica, the acidity of said dispersion being sufficient to prevent gelation.

20 2. The method according to claim 1 wherein the pH of said binder is about 2.7 to 5.4

3. The method according to claim 1 wherein the pH of said binder is about 3.6 to 4.4

4. The method according to claim 1 wherein the
25 ratio of refractory to binder is more than 2 to 1 on a weight basis.



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5 5. The method according to claim 1 wherein the refractory material comprises one or more of quartz, fused silica, monoclinic zirconia, stabilized electrically fused zirconia, mullite, aluminosilicates, calcined alumina, fused alumina, ceria or yttria.

6. The method according to claim 1 wherein the refractory material comprises one or more of alumina, ceria, zirconia or yttria.

10 7. The method according to claim 1 wherein the shell mold comprises two coats of refractory, each coat being bonded with said binder and said shell mold being supported by a solid mold structure.

15 8. The method according to claim 1 wherein the shell mold comprises one coat of refractory, said coat being bonded with said binder and said shell mold being supported by a solid mold structure.

20 9. The method according to claim 1 wherein the shell mold comprises one coat of refractory bonded with alumina being supported by an additional shell structure employing a different binder than said alumina.

10. The method according to claim 1 wherein the expendable pattern is a wax pattern.

25 11. The method according to claim 1, wherein after step e., the expendable pattern is removed from said shell mold.

12. The mold produced by the method of claim 1.



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13. In a method for producing castings of alloys having directionally solidified grains wherein a molten alloy is poured into a shell mold, the improvement which comprises employing as the shell mold that of claim 12.

5 14. The method according to claim 13 wherein the alloy comprises nickel and cobalt and one or more of hafnium, zirconium, tungsten, aluminum, titanium, niobium, molybdenum, carbon, silicon, manganese or yttrium.

10 15. The method according to claim 13 wherein the alloy comprises nickel or cobalt and one or more of zirconium, aluminum or titanium.

15 16. The method according to claim 13 wherein the mold is heated to 2000°F to 3100°F prior to pouring the molten alloy therein.

17. The method according to claim 13 wherein the mold is heated to 2750°F to 3100°F prior to pouring the molten alloy therein.

20 18. The method according to claim 13 wherein the refractory comprises one or more of alumina, ceria, zirconia and yttria.

25 19. In a method for casting an alloy comprising pouring a molten alloy in a shell mold, the improvement which comprises employing a mold having a surface comprising a non-fibrous alumina bonded refractory.



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20. The method according to claim 19 wherein the mold is preheated to an elevated temperature prior to pouring molten alloys therein.

21. The method according to claim 20 wherein
5 the mold is heated to 2000 to 3100°F prior to pouring the molten alloy therein.

22. The method according to claim 20 wherein the mold is heated to 2750°F to 3100°F prior to pouring the molten alloy therein.

10 23. The method according to claim 19 wherein the refractory comprises one or more of alumina, ceria, zirconia and yttria.

24. In a method of making a refractory coating comprising a binder and a refractory material, the
15 improvement wherein said binder comprises an essentially non-fibrous, aqueous, acidic dispersion of aluminum monohydrate, the amount of said acid in said dispersion being sufficient to prevent gelation.

25. The refractory coating produced by the
20 method of claim 24.



INTERNATIONAL SEARCH REPORT

W0 80/00134

International Application No PCT/US79/00446

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. B22C 9/04; B28B 7/34		
U.S. CL. 164/25, 26, 41, 42; 106/38.2, 38.22, 38.3, 38.9		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
U.S.	164/25, 26, 41, 42; 106/38.2, 38.22, 38.3, 38.9	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,722,577, Published 27 March 1973, Column 6, lines 26-34, Webb.	1-25
X	US, A, 3,935,023, Published 27 January 1976, Derolf.	1-25
X	US, A, 3,933,190, Published 20 January 1976, Fassler et al.	12-23
X	US, A, 3,752,689, Published 14 August 1973, Column 5, Lines 15-21, Moore, Jr.	1-25
A	US, A, 3,859,153, Published 07 January 1975, Beyer et al.	1
A	US, A, 3,894,572, Published 15 July 1975, Moore, Jr.	1
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
15 August 1979	16 OCT 1979	
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ISA/US	J. REED BATTEN, JR.	