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(54) Title: NOVEL COMPOSITIONS AND METHOD FOR NEUTRALIZATION AND SOLIDIFICATION OF HAZARDOUS ALKALI SPILLS

(57) Abstract

A dry particulate composition containing an organic neutralizing acid and, materials having varying absorption rates may be used to neutralize alkaline spills, and solidify the spills to render them harmless. These compositions may be applied to the spills by fire-extinguisher-like delivery devices which spread the compositions on the spills from a relatively safe distance without splattering the hazardous materials.

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NOVEL COMPOSITIONS AND METHOD FOR NEUTRALIZATION AND SOLIDIFICATION OF HAZARDOUS ALKALI SPILLS

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of U.S. Serial No. 06/859,122, which is hereby incorporated herein by reference.

1. Field of the Invention

This invention relates to novel compositions and the novel methods of their use for neutralization and clean-up of hazardous alkali spills.

2. Prior Art

Various compositions have been known in the past to be useful for the neutralization of alkali waste materials. Some prior art references describe methods for neutralizing alkali spills. However, these prior art compositions and methods for alkali waste neutralization entail certain disadvantages in situations in which alkali compositions spill in an industrial plant or similar cases.

United States Patent No. 3,042,622 (Kirschenbauer) describes an abrasive cleaning composition comprising a mixture of a water-insoluble

abrasive cleaning composition comprising a mixture or a water-insoluble abrasive material and an alkaline ingredient, and an acidic ingredient. The composition exhibits both alkaline and acidic cleansing properties in water. The abrasive agents used in the composition include siliceous materials including silex, tripoli, pumice, volcanic ash, pumicite, bentonite, diatomaceous earth, feldspar and the like. The composition may also include a water-soluble acidic ingredient, including citric acid (column 2, line 45). These abrasive compositions may be used for cleaning, such as in scouring powders, and for the removal of stains from metal surfaces. However, these compositions are useful as abrasives for cleansing, and cannot be applied to hazardous spill control.

United States Patent No. 3,708,429 describes cleaning compositions comprising a substantially anhydrous mixture of (a) a surface active agent, (b) an alkaline catalyst, (c) an acid release agent, and (d) a lower aliphatic alcohol. The acid release agent can be encapsulated using an encapsulating material which is stable in the anhydrous composition, but which dissolves or disperses in water in order to activate the acidic material inside. The acid release agents useful in this composition includes citric acid, glutaric acid and tartaric acid, as well as acid salts. This patent also states that the acidic materials may be absorbed onto solid carrier materials, e.g. acetic acid absorbed onto bentonite. These compositions are described as being useful for cleaning fatty soil from dishes and for dishwashing compositions which are used diluted in water, rather than for hazardous spill neutralization.

United States Patent No. 4,105,576

(Seidenberger) is directed to the control and clean-up of liquid caustic spills by neutralization and absorption into a granular composition formed from citric acid, expanded perlite, flour, fumed silica, a pH indicator dye and water. The composition is prepared by adding the pH indicator to deionized water, charging a blender with citric acid monohydrate through a crusher to break up lumps, and charging the blender with perlite. The pH indicator solution is poured in a substantially even fashion over the surface of the perlite and the components mixed for about twenty minutes. Flour is added to the mixture and blended such that the flour coats and partially dries the formulation. Fumed silica is then added and the composition blended to provide a homogeneous blend. The blend is then ready to absorb caustic spills. However, this method produces particles which are unsuitable for application to the spill from a safe distance.

SUMMARY OF THE INVENTION

This invention is directed to a novel composition and method of using the composition to neutralize and solidify hazardous alkali spills so as to prevent the spread of such a spill by absorption, neutralization and solidification from a safe distance away from the spill. The compositions of this invention limit the absorption rate so as to enable the maximum amount of alkali material to react and be neutralized.

The mode of application of the method of this invention allows the control and neutralization of hazardous spills from a distance without causing splashing of the hazardous materials during neutralization.

The novel compositions of this invention

contain the following: about 45 to 75% organic neutralizing acid, about 15 to 45% highly absorptive clay, about 10 to 45% less absorptive clay and about 0.5 to 10% weak water-soluble acid.

The novel compositions of this invention may be applied to a hazardous acidic spill through a delivery device similar to a fire extinguisher. The compositions are in the form of small particles of varying sizes, but within a narrow size distribution. Preferably, they have a predominant size distribution in the range between -40 to +200 Tyler screen mesh range.

The compositions of this invention may be made by mixing the components in a blender.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The compositions of this invention preferably contain between about 45 and about 80% by weight of organic neutralizing acid in a dry particulate form such as citric acid, fumaric acid, tartaric acid or benzoic acid, between about 5 to about 45% by weight of a highly absorptive clay such as attapulgite, perlite, fullers earth or minugel and the like, between about 10 to about 45% by weight of less absorptive clay, such as attapulgas clay and the like and between about 0.5 and about 10% by weight of weak water soluble acid such as sodium dihydrogen phosphate.

The organic neutralizing acid component of the compositions of this invention serve to neutralize, absorb and solidify the alkali spills to which they are applied. After treatment, they are amenable to safe clean-up. The organic neutralizing acid may be any organic acid which is in a dry particulate form at room temperature, such as citric acid, tartaric acid, benzoic acid or fumaric acid or

a combination of such acids. Such acids are relatively insoluble. Dry particulate acids are preferable so that the composition may be dispensed readily from a distance in a fire extinguisher-like delivery device in the appropriate dispersion pattern.

The absorptive clays which are present in the composition aid in absorbing and containing the hazardous alkaline materials so as to allow the acid component to react with and neutralize them. Preferably, different clays having varying degrees of absorption rates should be used so that the largest possible proportion of the alkaline materials may be given the opportunity to react and neutralize. Hence, a highly absorptive and a less absorptive clay component should be used in the composition. Highly absorptive clays include Minugel-200^{R}, some attapulgites, perlites and fullers earth. Less absorptive clays include certain attapulgas clays and the like.

A small amount of weak, water-soluble acid in the compositions of this invention functions to produce heat by reacting with the bases in the spill to allow the organic neutralizing acid to react more readily (these reactions provide heat of neutralization for the citric acid/hazardous alkali reaction). Because the spill may be absorbed quickly and thus be removed from the areas where it may freely react with the neutralizing acid, a small amount of weak, water soluble acid is desirable to increase the speed of reaction. This acid also generates some heat by reacting with the alkaline materials in the spill, thus providing the heat of solubilization for the sparingly-soluble organic neutralizing acids and increasing their opportunities to react with the base.

Dyes may be added to exemplify the

neutralization reaction as it progresses.

The compositions of this invention are preferably applied to the hazardous spills from a fire-extinguisher-like vessel. They are preferably applied in the dry form in which they are stored. They may be stored under pressure until used in a stored pressure vessel or they may be stored in an unpressurized vessel and pressurized by external gas through an external expellent gas cartridge.

The size distribution of the particles of the compositions of this invention allows them to be applied to spills in a "soft" pattern, i.e. relatively spread out such that they cover a spill as it spreads without splattering the spill. The compositions should be applied from a distance of about 10 to 15 feet. The nozzle velocity should be between about 30 and 50 feet/second. In order to achieve this velocity, the particles should have a size distribution between -40 and +200 Tyler screen mesh size.

The particulate compositions of this invention may be applied on a nitrogen gas stream. The particular specified size distribution will substantially assure the appropriate flow rate and delivery pattern.

The compositions of this invention contain both relatively less reactive organic acids and weak water soluble acids such as sodium dihydrogen phosphate. The sodium dihydrogen phosphate, for example, acts as a catalyst to aid the neutralization reactions. This encourages neutralization of many alkali materials which may have a higher heat of neutralization than others. This allows a controlled and complete neutralization reaction.

EXAMPLES

The following Examples set forth various compositions of this invention which can be used to neutralize, absorb and solidify alkali spills. They serve to illustrate, but not to limit the claimed invention.

Example 1	
69.5%	Citric Acid
15.0%	Fullers Earth
15.0%	Minugel 200
0.5%	Magnesium Stearate

Example 2	
75.0	Citric Acid
6.0%	Fullers Earth
18.5%	Minugel 200
0.5%	Magnesium Stearate

Example 3	
70.0%	Citric Acid
7.5%	Fullers Earth
22.5%	Minugel 200
4.09	gm Red dye #60

Example 4	
75.0%	Citric Acid
6.5%	Fullers Earth
18.5%	Minugel 200
6.81	gm Red dye #60

Example 5	
80.0%	Citric Acid
10.0%	Fullers Earth
10.0%	Minugel 200

Example 6	
70.0%	Citric Acid
22.5%	Fullers Earth
7.5%	Minugel 200

Example 7	
80.0%	Citric Acid
9.8%	Fullers Earth
9.8%	Minugel 200
0.4%	Magnesium Stearate

Example 8	
80.0%	Citric Acid
9.8%	Fullers Earth
9.8%	Minugel
0.4%	TCP

Example 9	
80.0%	Citric Acid
9.25%	Fullers Earth
9.25%	Minugel 200
1.5%	TCP

Example 10	
75.0	Citric Acid
6.0%	Fullers Earth
18.5%	Minugel 200
1.5%	TCP

Example 11	
75.0%	Citric Acid
6.5%	Fullers Earth
15.5%	Minugel 200
3.0%	TCP

Example 12	
75.0%	Citric Acid
6.5%	Fullers Earth
18.0%	Minugel 200
0.5%	TCP

Example 13	
80.0%	Citric Acid
10.0%	Fullers Earth
10.0%	Minugel 200
0.5%	Aluminum Octoate

Example 14	
80.0%	Citric Acid
9.75%	Fullers Earth
9.75%	Minugel 200
0.5%	Sodium Stearate

Example 15	
80.0%	Citric Acid
9.75%	Minugel 200
9.75%	Attapulgas Clay
0.5%	Aluminum Octoate

Example 16	
80.0%	Citric Acid
14.2%	Fullers Earth
5.3%	Attapulgas Clay
0.5%	Aluminum Octoate

Example 17

80.0% Citric Acid
9.75% Minugel 200
9.75% Attapulgas Clay
0.5% Aluminum Octoate

Example 18

80.0% Citric Acid
16.56% Attapulgite Clay
3.0% Starch
0.5% Polyacrylate

Example 19

80.0% Citric Acid
19.5% Attapulgite Clay
0.5% Polyacrylate

Example 20

60.0% Citric Acid
20.0% Fumaric Acid
19.5% Attapulgite Clay
0.5% Polyacrylate

Example 21

40.0% Citric Acid
40.0% Fumaric Acid
19.5% Attapulgite Clay
0.5% Petro AGS (mono-sodium salt of dimethyl naphthalene sulfonate)

Example 22

20.0% Citric Acid
60.0% Fumaric Acid
19.5% Attapulgite Clay
0.5% Petro AGS

Example 23

80.0% Fumaric Acid
19.5% Attapulgite Clay
0.5% Petro AGS

Example 24

65.0% Citric Acid
18.0% Fumaric Acid
15.0% Attapulgite Clay
2.0% Starch (grain product, modified starch and polyacrylate crystals known commercially as "S-500")
0.5% Petro AGS

Example 26

60.0% Citric Acid
19.0% Fumaric Acid
1.0% Starch
19.5% Attapulgite Clay
0.5% Petro AGS

Example 27

70.0% Citric Acid
7.5% Fullers Earth
22.5% Minugel 200

Example 28

80.0% Citric Acid
10.0% Fullers Earth
10.0% Minugel 200

Example 29

70.0% Citric Acid
22.5% Fullers Earth
7.5% Minugel 200

Example 30

80.0% Citric Acid
9.8% Fullers Earth
9.8% Minugel 200
0.4% Mg Stearate

Example 31

80.0% Citric Acid
9.25% Fullers Earth
9.25% Minugel 200
1.50% Tricalcium Phosphate (TCP)

Example 31

80.0% Citric Acid
9.8% Fullers Earth
9.8% Minugel 200
0.4% TCP

Example 32

75.0% Citric Acid
6.0% Fullers Earth
18.5% Minugel 200
0.5% Mg Stearate

Example 25

60.0% Citric Acid
18.0% Fumaric Acid
2.0% Starch
19.5% Attapulgite Clay
0.5% Petro AGS

Table I below sets forth the results of tests demonstrating the ability of the compositions of the foregoing Examples 1-17 to absorb, neutralize and solidify alkali spills. In these tests, a specified amount of alkaline material was spilled in an enclosed area. The type of alkali is set out in column 2 of Table I, entitled "Base". The volume of spill is set out in column 3, entitled "Volume (gal)". The compositions of this invention were then applied from a fire extinguisher type dispenser. The inital weight of the neutralize composition, or of "agent", was measured prior to the test and is set forth in column 4 in (pounds)-(ounces). The weight of agent actually discharged was measured after the test, which depends on the size distribution of the particles, is set forth in column 5 entitled "Weight Discharge". The percent discharge measures the efficiency of the discharge, column 6. The inital pH of the alkali spill measured after dispensing the agent is in column 7. The final pH of the agent/alkali spill mixture was measured after the test reaction took place (column 8). Comments regarding the quality of the resulting solid and the reaction between the composition and alkali material are set forth in column 9.

Table II sets forth average particle size distributions for several of the compositions of this invention.

TABLE I

Example	Base	Volume (gal)	Wt. Agent	Wt. Discharge	% Discharge	pH(i)	pH(f)	Solid
1	NaOH	2	24 - 9	22 - 13	92.9	12.70	12.83	soft mud; good absorption; fast reaction
2	NaOH	2	24 - 8	23 - 12	96.9	12.67	12.99	Poor absorption until mixed; fast complete reation
3	NaOH	2	24 - 4	23 - 1	95.2	13.09	12.94	Solid after setting up
3A	NaOH	2	24 - 8	23 - 8	95.9	8.46	10.57	Liquid until mixed - nice solid; fast, good reation
3B	NaOH	2	23 - 4	--	100	11.83	13.27	Applied with shovel
4	NaOH	1.8	24 - 8	23 - 6	95.4	12.6	12.65	Solidified with time; fast reaction
4A	KOH	1.86	24 - 4	23 - 0	94.8	6.05	5.78	Fast, complete reaction; moderate heat; poor absorption;
3C	NaOH	1.68	24 - 8	23 - 8	95.9	10.07	10.63	Soupy until mixed; good absorption; fast reaction
3D	NaOH	1.80	24 - 8	23 - 4	94.9	12.25	12.30	Good absorption; fast reaction
5	NaOH	1.86	24 - 8	23 - 2	94.4	11.40	11.41	Poor at end of discharge
5A	KOH	1.78	24 - 8	22 - 2		4.93	4.72	Liquid in pan - little solid; fast reaction
6	KOH	1.97	23 - 6	21 - 8	92.0	5.95	5.75	Very poor discharge; fast reaction; poor absorption
7	NaOH	1.90	24 - 8	22 - 10	92.3	--	--	No reaction
7A	NaOH	1.98	24 - 8	23	93.9	--	--	No reaction

TABLE I (continued)

Example	Base	Volume (gal)	Wt. Agent	Wt. Discharge	% Discharge	pH(i)	pH(f)	Solid
8	NaOH	1.83	24 - 8	22 - 2	90.3	6.67	6.78	Reacted before beginning stir; good absorption and reaction
9	NaOH	1.91	24 - 8	22 - 11	92.6	12.47	12.43	Poor flow at end of discharge; good absorption and reaction
10	NaOH	1.90	24 - 8	23 - 2	94.4	11.59	12.19	Poor flow at end of discharge; good absorption and reaction
11	NaOH	1.81	24 - 8	22 - 6	95.4	10.06	9.12	Solid very hard when dry; good absorption and reaction
12	NaOH	1.76	26 - 2	24 - 10	94.3	12.16	12.60	Fast reaction - not hot; good absorption
12A	NH_4OH	2.05	23 - 12	22 - 14	96.3	4.05	3.94	Cut off ammonia vapors; fast reaction; poor absorption
13	NaOH	2.04	23 - 11	22 - 3	93.67	12.19	12.50	Better discharge; dustier than minugel; fast, non-violent reaction
14	NaOH	2.01	24 - 8	15 - 10	63.78	12.45	12.76	High reaction of short duration
15	NaOH	1.98	25 - 10	24 - 0	93.7	10.22	10.19	Good range, reacted before mix; non-violent; and absorption
15A	KOH	1.71	23 - 15	22 - 1	92.2	4.75	4.52	Good range; relatively fast, mild reaction

TABLE I (continued)

Example	Base	Volume (gal)	Wt. Agent	Wt. Discharge	% Discharge	pH(i)	pH(f)	Solid
16	NaOH	2.05	25 - 10	23 - 10	92.2	5.42	5.42	Flow dropped off at end; fast, mild reaction
17	NaOH	2.08	25 - 12	24 - 5	94.4	12.35	12.73	Good discharge; good reaction and absorption
17A	KOH	2.15	25 - 11	24 - 5	94.7	4.02	4.05	Fast, mild reaction; poor absorption
17B	NH_4OH	2.19	26 - 6	25 - 0	94.8	6.83	6.93	Slight drop in range, no ammonia smell
17C	KOH	2.59	26 - 2	--	--	5.58	5.60	Good discharge; good reaction; poor absorption
17D	KOH	2.96	26 - 0	24 - 10	94.7	6.75	6.67	Good discharge; good reaction; poor absorption
17E	KOH	3.31	26 - 0	24 - 12	95.2	12.81	12.90	Good discharge; good reaction
17F	NH_4OH	2.47	26 - 0	24 - 8	94.7	4.59	4.60	No ammonia odor after application; fast reaction, poor absorption
17G	NH_4OH	3.09	25 - 8	23 - 14	93.6	4.80	4.78	Fast reaction
18	NaOH	-	-	-	-	9.5	5.85	Good
19	NaOH	-	-	-	-	5.85	5.9	Good - wet solid.
20	NaOH	-	-	-	-	12.5	9.1	Good - mild reaction - wet solid.
21	NaOH	-	-	-	-	9.01	4.95	Good soak up - wet solid - no visible rxn.
22	NaOH	-	-	-	-	12.28	4.95	Good soak up - wet solid - no visible rxn.

TABLE I (continued)

Example	Base	Volume (gal)	Wt. Agent	Wt. Discharge	% Discharge	pH(i)	pH(f)	Solid
23	NaOH	-	-	-	-	11.4	4.49	Good soak up - wet solid - no visible rxn.
24	NaOH	-	-	-	-	11.9	5.62	Very good dry solid, good rxn. and good soak up.
25	NaOH	-	-	-	-	7.8	5.5	Very dry, spongy solid, good soak up and good rxn.
26	NaOH	-	-	-	-	12.0	9.1	Wet solid, good soak-up and good reaction.
27	NaOH	2	23.06	-	95.9	13.09	12.94	Poor initial absorption until mixed; very liquid - solid after setting up; faster rxn. without magnesium stearate.
28	NaOH	1.86	23.2	-	93.4	11.41	13.5	Very poor discharge, no distance; liquid in pan, little solid.
29	NaOH	1.95	23.375	-	92	5.75	13	Very poor discharge, no flow at end-long discharge time-stearate needed for flow to stop leaks.
30	NaOH	1.9	24.5	-	92.3	-	-	No reaction
31	NaOH	1.83	24.5	-	90.3	6.78	14	Heat during discharge reacted before beginning to stir.
32	NaOH	1.91	24.5	-	92.6	12.47	12.43	Nozzle leaked.

TABLE II

Example	% Citric Acid		Sieve Size 20	40	100	200	325	PAN	BULK DENSITY
11	75		--	7.94	82.25	5.23	1.65	2.92	110
14	80		--	8.86	86.24	3.10	0.24	1.56	120
12	75		--	4.79	69.32	9.30	4.55	12.04	117
13	80		--	8.03	84.49	3.99	0.66	2.83	119
B12A-1	80		--	4.72	89.50	3.58	0.28	1.92	113
		(AVERAGE DISCHARGE)							
15	80	92.95	--	3.97	83.06	6.56	1.30	5.11	116
17	80	94.63	0.02	9.98	76.45	6.90	0.84	5.80	114
17A	80	94.7	0.02	8.04	78.04	7.15	2.54	4.24	116
17F	80	93.97	--	3.98	80.78	6.53	2.61	6.10	118
	OVERALL	94.08							
25A	65		0.06	18.56	76.3	3.5	1.5	0.90	126

WHAT IS CLAIMED IS:

1. A composition for neutralizing and solidifying hazardous alkali spills comprising about 45 to 80% organic neutralizing acid, about 5 to 45% highly absorptive clay, about 10 to 45% less absorptive clay and about 0.5 to 10% weak water-soluble acid.

2. A composition according to claim 1 wherein organic neutralizing acid is in a dry particulate form and is selected from the group consisting of citric acid, tartaric acid, fumaric acid and benzoic acid.

3. A composition according to claim 1 wherein said highly absorptive clay is selected from the group consisting of attapulgite, perlite, fullers earth and minugel.

4. A composition according to claim 1 wherein said less absorptive clay is attapulgas clay.

5. A composition according to claim 1 wherein said weak water soluble acid is selected from the group consisting of sodium dihydrogen phosphate, magnesium stearate, sodium stearate and aluminum octoate.

6. A composition according to claim 1 comprising between about 60 and 80% by weight of organic neutralizing acid, between about 5 and 15% highly absorptive clay, between about 10 and 20% less absorptive clay and between about 0.5 and 1% weak water soluble acid.

7. A composition for absorbing neutralizing and solidifying alkali spills comprising about 80% by weight citric acid, about 9.75% minugel, about 9.75% attapulgas clay and about 0.5% aluminum octoate.

8. A method of neutralizing and solidifying hazardous alkali spills comprising applying a composition to the spill comprising about 45 to 75%

organic neutralizing acid, about 15 to 45% highly absorptive clay, about 10 to 45% less absorptive clay and about 0.5 to 10% weak water-soluble acid such that the spill is neutralized and solidified.

9. A method according to claim 2 wherein said application is accomplished by delivering said composition to said spill under pressure on a nitrogen gas propellant from a fire-extinguisher-like delivery device.

10. A composition according to claim 1 which is in the form of dry particles having a size distribution between -40 and +200 Tyler screen mesh size range.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/00991

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC [4] G21F 9/14, 9/16; C09D 1/02,06; C04B 7/02

U.S.C.L. 252/628, 631, 192, 193; 106/74, 78, 89, 97, 98, Dig. 4

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	252/626, 628, 631, 189, 190, 193, 8; 210/681, 682, 751 169/9, 45, 46, 47, 71 106/74, 78, 97, 98, Dig. 2, Dig 4; 134/3, 28

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

LEXPAT 1975→DATE
USPAT 1975→DATE

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]
Y	US, A, 4,524,835 Published 25 June 1985, (Mingrone) (see entire document	1-10
A	US, A, 4,249,949 Published 10 February 1981, (Woolier)	1-10
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A	US, A, 3,980,588 Published 14 Septemeber 1976, (Thompson)	1-10

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
25 June 1987	07 JUL 1987
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Howard J. Locker HOWARD J. LOCKER EXAMINER GROUP ART UNIT 223

Form PCT/ISA/210 (second sheet) (May 1986)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	US, A, 3,837,872 Published 24 September 1974, (Conner)	1-10
A	US, A, 3,708,429 Published 02 January 1973, (Hall)	1-10
A	US, A, 3,196,106 Published 20 July 1965, (Haden, Jr. et al)	1-10
Y	US, A, 3,090,749 Published 21 May 1963, (Warnock) (see entire document)	1-10
A	US, A, 3,042,622 Published 03 July 1962, (Kirschenbauer)	1-10