PCT WORLD INTELLECTUAL PROPE
International Bu

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9607763A1

(51) International Patent Classification 6 :
C22B 26/20, B08B 7/00, E21B 37/00

A1

(11) Int

(43) International Publication Date: 14 March 1996 (14.03.96)

(21) International Application Number: PCT/US95/09239

(22) International Filing Date: 21 July 1995 (21.07.95)

(30) Priority Data:
303,907 9 September 1994 (09.09.94) US

(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventors: MORRIS, Richard, Leo; 202 N. Venice, Duncanville, TX 75116 (US). PAUL, James, Mark; 128 Williams, Desoto, TX 75115 (US).

(74) Agents: MILLER, Lawrence, O. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

(81) Designated States: CA, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD FOR REMOVING ALKALINE SULFATE SCALE

(57) Abstract

The present invention relates to the use of solvents and low frequency sonic energy within the range of 1.5 to 6.5 KHz, preferably less than 2.0 KHz and most preferably 1.25 KHz, for enhancing the dissolution of alkaline earth metal scales from wel bores using a scale-removing solvent comprising an aqueous alkaline solution having a pH of 8 to 14 and containing EDTA or DTPA and a catalyst or synergist, preferably an oxalate anion. When the scale deposit is contacted with the scale removing solvent while simultaneously transmitting low frequency sonic energy through the solvent, substantially more scale is dissolved at a faster rate than previously possible.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

METHOD FOR REMOVING ALKALINE SULFATE SCALE

This invention relates to the use of solvents and low frequency sonic energy for enhancing the dissolution of alkaline earth metal scale, particularly strontium and barium sulfate scale, from surfaces with scale deposits on them using a scale-removing solvent. It is particularly useful for the removal of such scale from oil field equipment including downhole pipe, tubing and casing as well as subterranean formations. It is also applicable to the removal of these scale deposits from other equipment such as boilers and heat exchangers.

Many waters contain alkaline earth metal cations, such as barium, strontium, calcium, magnesium and anions, such as sulfate, bicarbonate, carbonate, phosphate and fluoride. When combinations of these anions and cations are present in concentrations which exceed the solubility product of the various species which may be formed, precipitates form until the respective solubility products are no longer exceeded. For example, when the concentrations of the barium and sulfate ions exceed the solubility product of barium sulfate, a solid phase of barium sulfate will form as a precipitate. Solubility products are exceeded for various reasons, such as evaporation of the water phase, change the pH, pressure or temperature and the introduction of additional ions which can form insoluble compounds with the ions already present in the solution.

As these reaction products precipitate on the surfaces of the water-carrying or water-containing system, they form adherent deposits or scale. Scale may prevent effective heat transfer, interfere with fluid flow, facilitate corrosive processes, or harbor bacteria. Scale is an expense problem in any industrial water system, in production systems for oil and gas, in pulp and paper mill systems, and in other systems, causing delays and shutdowns for cleaning and removal.

In our U.S. Patent Nos. 4,980,077, 4,990,718, 5,049,297, 5,084,105, and 5,093,020, there is disclosed a method for removing barium sulfate and other sulfate scales by a solvent comprising a combination of a chelating agent comprising polyaminopolycarboxylic acid such as EDTA or DTPA together with a catalyst or synergist comprising anions of (1) a monocarboxylic acid such as acetic acid, hydroxyacetic acid, mercaptoacetic acid or salicylic acid; (2) oxalates; (3) thiosulfates; (4) nitriloacetic acid; (5) fluoride; (6) persulfate; (7) hypochlorite or (8) carbonate. The scale is removed under alkaline conditions, preferably at pH values of 8.0 to 14.0, with best results being achieved at pH 12. When the solvent becomes saturated with scale metal cations, the spent solvent is disposed of by re-injection into the subsurface formation or regenerated.

It is common practice when using scale dissolvers to pump a slug or volume of solvent into the well and leave it to stand static for a long period of time. This is not effective from an economic stand point because the well must be shut in for long periods of time, resulting in loss of production. Soaking is also not an efficient method from a reaction rate standpoint. Also, circulating scale solvent into the well bore is too costly, due to the large volume of solvent needed to fill the tubing and allow circulation.

This invention provides an effective method for removing alkaline earth metal scales by contacting the scale with a scale-removing solvent while simultaneously transmitting sonic energy through the solvent having a low frequency to more effectively dissolve the scale.

A method for removing alkaline earth sulfate scale comprising contacting the scale with an aqueous solution having a pH of 8 to 14 and comprising a chelating agent comprising a polyaminopolycarboxylic acid present in a concentration of from 0.1 M to 1.0 M or salt of such an

acid and a synergist or catalyst and simultaneously transmitting sonic energy through the solvent having a low frequency, in the range of 1.5 to 6.5 KHz, preferably less than 2.0 KHz and most preferably 1.25 KHz. The preferred synergist or catalyst is the oxalate anion but other synergists may also be used including monocarboxylate acid, thiosulfate or nitriloacetic acid synergists. The concentration of the synergist or catalyst is in the range of 0.1 M to 1.0 M.

Figures 1-4 illustrates the rate of dissolution of barium sulfate using a solvent containing 0.5 M DTPA and 0.5 M oxalic acid at a pH of 12.2 while simultaneously transmitting sonic energy through the solvent having various low frequencies and a power level of 6 (60% of power).

Figure 5 illustrates the rate of dissolution of barium sulfate using a solvent containing 0.5 M DTPA and 0.5 M salicylic acid at a pH of 12.2 while simultaneously transmitting sonic energy through the solvent at a frequency of 1.5 KHz and a power level of 6 (60% of power).

Figure 6 illustrates the rate of dissolution of barium sulfate in field tubing using a DTPA/oxalic acid solvent while simultaneously transmitting sonic energy through the solvent having a frequency of 1.5 KHz and a power level of 6 (60% of power).

Figure 7 illustrates the rate of dissolution of strontium sulfate in field tubing using a DTPA/oxalic acid solvent and simultaneously transmitting sonic energy through the solvent containing solvent having a frequency of 1.5 KHz and a power level of 6 (60% of power).

Figure 8 illustrates the rate of dissolution of calcium sulfate in field tubing using a DTPA/oxalic acid solvent while simultaneously transmitting sonic energy through the solvent having a frequency of 1.5 KHz and a power level of 6 (60% of power).

Figure 9 illustrates the effect of sonic energy at a level of 1.25 KHz and 2.0 KHz on the rate of dissolution of barium sulfate using a DTPA/oxalic acid solvent at a power level of 6.5 and a pH of 12.

Figure 10 illustrates the effect of sonic energy at a level of 1.25 KHz and 2.0 KHz on the rate of dissolution of barium sulfate using a EDTA/oxalate acid solvent at a power level of 6.5 and a pH of 12.

According to the present invention, alkaline earth sulfate scales, especially barium sulfate, calcium sulfate and strontium sulfate scale, are removed by use of chemical scale-removing solvents subjected to low frequency sonic energy in the range of 1.5 to 6.5 kHz, preferably less than 2.0 KHz and most preferably 1.25 KHz.

The method is particularly useful for the removal of such scale from oil field equipment used to bring oil and/or water from subterranean formations to the surface. The method may, however, also be used to remove scale from the formations themselves, especially in the regions surrounding production and injection wells. Scales and deposits can form to such an extent that the permeability of the formation is impaired resulting in lower flow rates, higher pump pressures, and ultimately abandonment of the well. The method may also be used to remove scale from above-ground equipment both in the oil field and elsewhere, for example, from boilers and heat exchangers and other equipment exposed to scale-forming conditions.

The scale itself is usually in the form of an adherent deposit of the scale-forming mineral on metal surfaces which have been exposed to the water containing the scale-forming components. These components comprise alkaline earth metals including calcium strontium and barium, together with variable amounts of radium, depending upon the origin of the waters. Barium sulfate scale is particularly difficult to remove by existing chemical methods in view of its very low solubility.

The present invention removes the scale deposits with an aqueous solvent comprising a chelating agent and a catalyst or synergist to speed up the dissolution of the scale as disclosed in U.S. Patent 4,980,077, referenced above, which issued on December 25, 1990 to J.M. Paul and R.L. Morris while simultaneously transmitting low frequency sonic energy through the solvent. This patent is hereby incorporated by reference. The pH of the solvent is maintained at pH values of 8.0 to 14.0, preferably at 11 to 13, and preferably 12. Suitable chelating agents comprise polyaminopolycarboxylic acid such as EDTA or DTPA which is intended to form a stable complex with the cation of the alkaline earth scale forming material. The chelant may be added to the solvent in the acid form or, alternatively, as a salt of the acid, preferably the potassium salt. The concentration of the chelant in the aqueous solvent should normally be in the range of 0.1 M to 1.0 M. The concentration of the catalyst or synergist in aqueous solvent will also be in the range of 0.1 M to 1.0 M. In any event the alkaline conditions used in the scale removal process will convert the free acid to the salt.

The preferred synergist or catalyst is the oxalate anion as described in our U.S. Patent 4,980,077 referenced above. The oxalate is preferably used in an amount of 0.1 to 1.0 M, preferably 0.5 M, with a pH of 8.0 to 14.0, preferably 11 to 13, and usually 12. The desired pH value is obtained by the addition of a base, preferably a potassium base such as caustic potash, potassium hydroxide. An alternative synergist or catalyst is a monocarboxylic acid anion, preferably salicylate, as described in our U.S. Patent 5,084,105, referenced above, which issued January 28, 1992, which patent is hereby incorporated by reference. The thiosulfate or nitriloacetic acid catalysts described in our U.S. Patent 5,049,297, referenced above, issued September 17, 1992,

may also be used which patent is hereby incorporated by reference. As described in our U.S. patent 5,093,020 referenced above, the catalyst may also be a fluoride, persulfate or hypochlorite anion. In addition, suitable catalysts may be selected from a member of the group consisting of carbonate, formate, amino acetate, hydroxy acetate and thioacetate anions. Generally these anions are added as salts or the free acid, depending on the stability and availability of the chosen synergist. In either case, however, the relatively alkaline conditions under which the process is operated, will result in the acid, if used, being converted to the salt form. The potassium salts are preferred in view of their greater solubility and for this reason, the solvent should preferably be brought to the desired pH value with a potassium base, preferably potassium hydroxide. The amounts of the chelant used with the monocarboxylic acid and other synergists are comparable to the amounts used with the oxalate synergists and comparable solution pH volume are also used, i.e. chelant and synergist concentration from 0.1 to 1.0 M, usually 0.5 M, solution pH from 8 to 14, usually 11 to 13 and for best results, 12.

The preferred solvents comprise 0.1 to 1.0 M of ethylenediaminetetraacetic acid (EDTA) or diethylene-triaminepentaacetic acid (DTPA), or salts of these acids, as a chelant. In addition, the preferred oxalate catalyst is added to the aqueous solution in 0.1 to 1.0, preferably up to 0.5 M. The pH of the solvent is then adjusted by the addition of a base to the desired value, preferably to pH 12. We have found that it is important to avoid the use of sodium cations when operating at high pH values, pH 8, and instead, to use potassium or, alternatively, cesium as the cation of the scale-removing agent. Potassium is preferred for economy as well as availability. Thus, the normal course of making up the solvent will be to dissolve

the chelant and the oxalic acid (or potassium oxalate) in the water to the desired concentration, after which a potassium base, usually potassium hydroxide is added to bring the pH to the desired value of 12. This aqueous composition can be used to remove scale from the equipment, or alternatively, pumped into the subterranean formation when it is the formation which is to be subject to descaling while in both cases simultaneously transmitting sonic energy having a low frequency through the solvent.

The scale removal is effected under alkaline conditions preferably at pH values of from 8.0 to 14.0, with optimum values being from 11 to 13, preferably 12. As noted above, the use of caustic potash is preferred to bring the composition to the desired pH since the potassium salts formed by its use are more soluble than the corresponding sodium salts.

The mode of operation of the synergist or catalyst is not presently understood. While not desiring to be bound to a particular theory concerning the actual mechanism of its activity in converting or dissolving the scale, it is believed that adsorption of the synergist or catalyst on the barium sulfate surface may modify the surface crystal structure in such a way that the barium in the modified crystal is easily removed by the chelating agent.

The aqueous solution containing the composition can be directed down a wellbore to remove barium sulfate scale which has fouled the tubular equipment e.g. piping, casing etc., and passage ways. Prior to being directed into the wellbore, the composition may be heated to a temperature between 25°C to 100°C, although the temperatures prevailing downhole may make pre-heating unnecessary. Once within the tubular goods and the passageways requiring treatment, sonic vibrations having a low frequency in the range of 1.5 to 6.5 KHz, preferably less than 2.0 KHz and most preferably 1.25 kHz, are transmitted

through the solvent. The low frequency sonic energy is generated by a suitable source containing a vibrator or transducer driven by electrical power that is lowered down the wellbore into the solvent. A suitable sonic energy source is manufactured under the trade designation "T"-Motor™ by Sonic Research Corporation that generates sonic vibrations having a frequency within the range of 1.25 to 6.5 KHz. The low frequency sonic energy excitation of the scale-removing solvent enables the solvent to more effectively dissolve the scale. Although it is not presently understood the mechanism of how low frequency sonic energy more effectively enables the solvent to dissolve the scale, it is believed that the sonic energy breaks the scale into smaller particles and also agitates the solvent to create a flushing action by the solvent relative to the scale. After the solvent remains in contact with the equipment for the desired time, the sonic energy is discontinued and the solvent containing the dissolved scale is produced to the surface and may be disposed of as required, possibly by re-injection into the subsurface formation. This procedure can be repeated as often as required to remove scale from the equipment.

In order to demonstrate the use of low frequency sonic energy for enhancing the scale dissolving capacities of scale-removing solvents, various aqueous solutions have been tested in laboratory tests the results of which are described in the discussions which follow. The experiments described below were carried out in cylindrical glass vessels. Barium sulfate or, when applicable, other sulfates or solid scale components, were agitated with the selected solvents while simultaneously transmitting sonic energy through the solvent having frequencies in the range of 1.5 to 6.5 KHz, preferably less than 2.0 KHz and most preferably 1.25 KHz, and the rates of dissolution and final dissolved concentrations determined. These tests were repeated with the same

solvents without the use of sonic energy. The results are reported graphically in the Figures.

As shown in Figures 1 to 4, the rate of dissolution of barium sulfate using an aqueous solvent containing 0.5 M DTPA and 0.5 M oxalic acid at a pH of 12.2 and a temperature of 25°C while simultaneously transmitting various low frequencies of sonic energy through the solvent at a power level of 6 (60% of power), is compared to the rate of dissolution using the same solvent without sonic energy (control). The rate of dissolution of barium sulfate in the solution is measured by the percent (%) transmittance of the dispersed barium sulfate scale contained in the solvent to light. The percent (%) transmittance of light increases in proportion to the amount of barium sulfate dissolved by the solvent. As shown in Figures 1 and 4, initially, percent (%) transmittance decreases (number of particle and/or surface area increases) for a short length of time and then it begins to increase at a higher rate. The reduction in percent (%) transmittance is believed to be a result of breaking apart agglomerations of barium sulfate crystals. The lower percent (%) transmittance is not observed in dispersions of barium sulfate in the absence of sonic energy. The results demonstrate that when sonic energy is transmitted through the solvent, there is a significant increase in the rate of dissolution of barium sulfate and the amount of barium sulfate dissolved.

Figure 5 shows the rate of dissolution of barium sulfate using an aqueous DTPA/salicylic acid solvent with and without low frequency sonic energy. The results show a significant increase in the rate of dissolution of barium sulfate and an increase in the amount of barium sulfate dissolved.

We also evaluated the rate of dissolution of barium sulfate, strontium sulfate and calcium sulfate scale in field tubing using sonic energy having a frequency of 1.5

KHz at a power level of 6 (60% of power) using a DTPA/oxalic acid solvent at 50°C and a pH of 12.2. Heavy scale and tar deposits were completely removed between 2 and 3 hours with sonic enhancement at 50°C. Most of the scale and tar remains after 6 hours with stirring only at 50°C. As shown in Figures 6 and 7, low frequency sonic energy improves dissolution of barium and strontrium sulfate scales (in the field tubing) by a factor of two. As shown in Figure 8, low frequency sonic energy improves dissolution of calcium sulfate scale in the field tubing by a factor of 1.75. These results show that the use of a solvent enhanced with low frequency sonic energy significantly increases the rate of dissolution of scale in field tubing compared to use of a solvent without sonic energy.

We also evaluated the effect of sonic energy frequency on the rate of barium sulfate at frequencies of 1.25 KHz and 2.0 KHz. As shown in Figure 9, the results show that there is a significant increase in the rate of dissolution of barium sulfate (amount of barium dissolved) by the aqueous DTPA solvent using the lower frequency of 1.25 KHz. As shown in Figure 10, the results show that there is a significant increase in the rate of dissolution of barium sulfate by the aqueous EDTA solvent up to forty (40) minutes for the lower frequency of 1.25 KHz and then dissolution tapers off to a constant value for both frequencies. These results show that the use of the lower frequency (1.25 KHz) significantly increases the rate of dissolution of barium sulfate scale using an aqueous DTPA sulfate scale using an aqueous DTPA or EDTA solvent when compared to the use of a frequency of 2.0 KHz.

The sonic energy for the above tests was generated by a "T" - Motor™ transducer manufactured by Sonic Research Corporation as discussed above. The T-Motor™ consists of a magnetostrictive material in the form of rods compressed together and wrapped with a wire coil. The rods comprise

90% iron, 5% terbium and 5% dysprosium sold under the trade designation "Terfenol D" by Edge Technologies, Inc. The Terfenol D rod is the only material known that can produce variable frequency, and withstand high temperature and pressure. The rods vibrate length wise when a DC current flows through the coil. The induced magnetic field causes the rods to expand and contract, i.e. magnetostrictive motion. This motion, or vibration, generates an acoustic wave or sonic energy having a frequency in the range of 0-50 KHz which extends forward from the T-Motor™ for some distance and the acoustic pressure wave is estimated at a magnitude of 3,000 psi. The T-Motor™ or transducer is powered by a standard frequency generator and a power amplifier. For all tests, the power level was set at 6 (60% of power). The frequency of the vibrations transmitted through the scale solvent for dissolving alkaline earth sulfate scale in the above tests was in the range of 1.5 to 6.5 KHz, preferably less than 2.0 KHz and most preferably 1.25 KHz. The T-Motor™ is only 60 cm. in length and 5 cm. in diameter and can easily be lowered down wellbore tubing for transmitting sonic energy through a scale-removing solvent contained in the wellbore.

Claims:

1. A method for removing alkaline earth scale in a wellbore penetrating a subterranean formation for the production of fluids comprising contacting the scale with an aqueous solution having a pH of 8 to 14 and comprising a chelating agent comprising a polyamino-polycarboxylic acid present in a concentration of from 0.1 M to 1.0 M or salt of such an acid, and a catalyst which comprises anions of organic or inorganic acids and mixtures thereof, where said acids have an ionization constant of less than 10^{-2} present in a concentration of from 0.1 to 1.0 M to dissolve the scale, transmitting sonic energy having a frequency in the range of 1.5 to 6.5 kHz through the aqueous solution and subsequently removing the dissolved scale from the wellbore, said sonic energy generated by a magnetostrictive transducer lowered into the wellbore.

2. A method according to claim 1 wherein the chelating agent comprises DTPA.

3. A method according to claim 1 wherein the pH of the solution is from 11 to 13.

4. A method according to claim 1 wherein the chelating agent comprises EDTA

5. A method according to claim 1 wherein the scale consists of barium, strontium or calcium sulfate and mixtures thereof and naturally occurring radioactive material (NORM), mainly radium 226 and radium 228.

6. A method according to claim 1 in which the scale comprises barium sulfate scale.

7. A method according to claim 1 in which the catalyst comprises thiosulfate, nitriloacetate, fluoride, formate, amino acetate, thioacetate, salicylate, carbonate, persulfate, thioacetate, hydroxy acetate, hypochlorite, and oxalate anions.

8. A method according to claim 1 in which the frequency of the sonic energy is less than 2.0 KHz.

9. A method according to claim 1 in which the frequency of the sonic energy is 1.25 KHz.

10. A method according to claim 1 in which the pH of the solution is 12.

11. A method according to claim 1 in which the solution is brought to the specified pH by the addition of a potassium base.

12. A method according to claim 1 in which the scale is contacted with the solution at a temperature from 25°C to 100°C.

FIG. 1

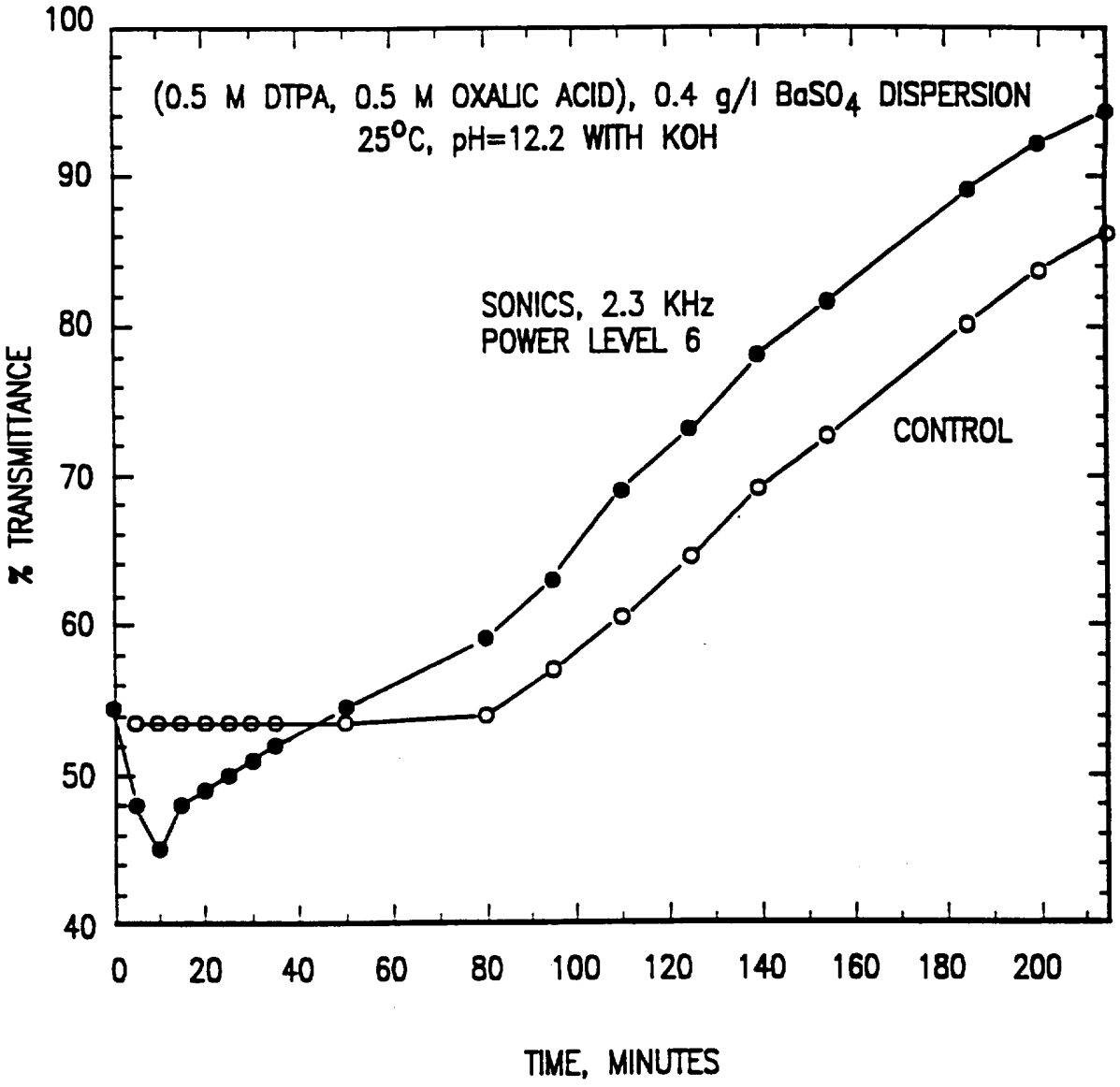

(0.5 M DTPA, 0.5 M OXALIC ACID), 0.4 g/l BaSO4 DISPERSION
25°C, pH=12.2 WITH KOH
SONICS, 2.3 KHz
POWER LEVEL 6
CONTROL
% TRANSMITTANCE
TIME, MINUTES
100
90
80
70
60
50
40
0
20
40
60
80
100
120
140
160
180
200

FIG. 2

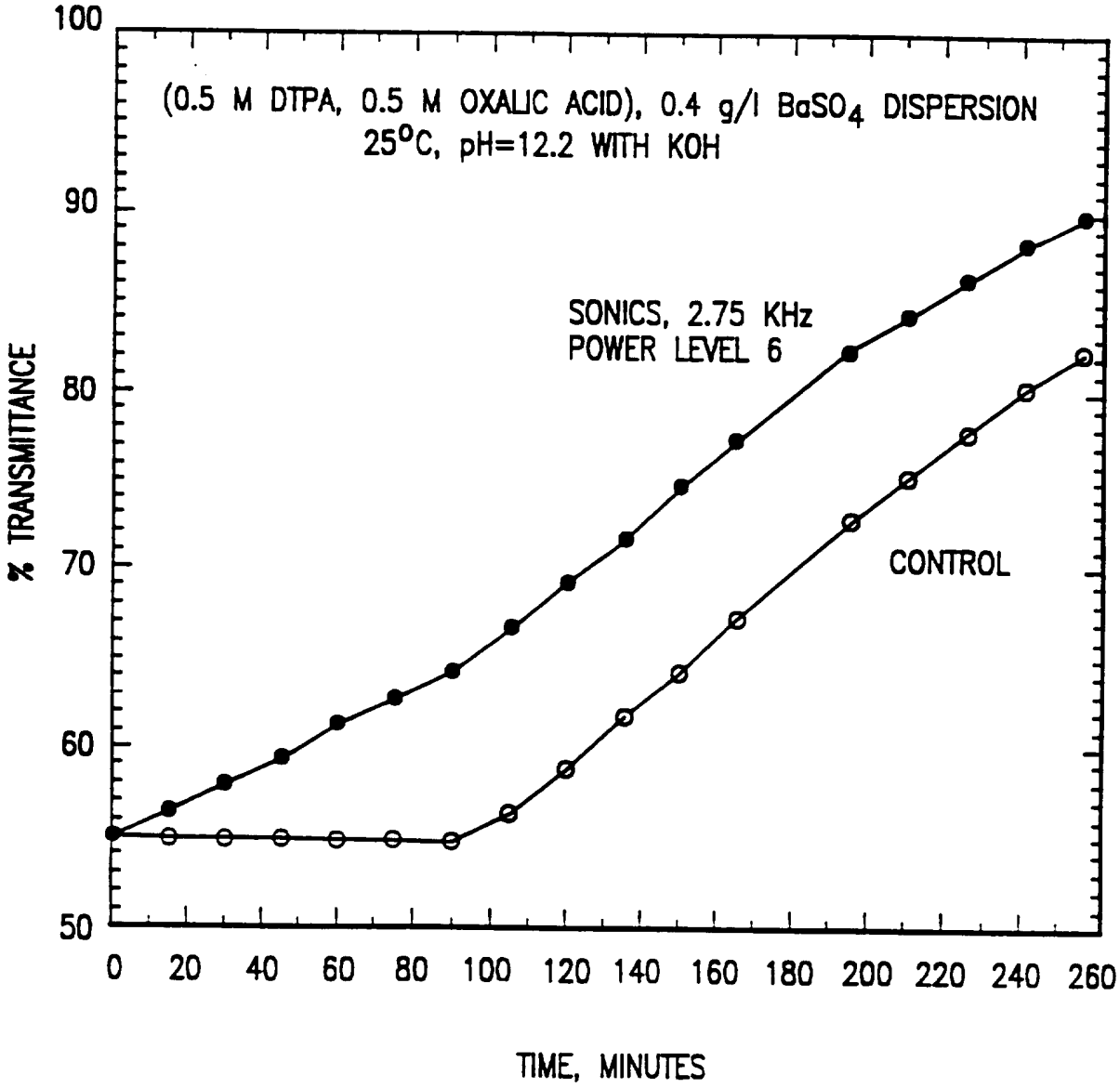

(0.5 M DTPA, 0.5 M OXALIC ACID), 0.4 g/l BaSO4 DISPERSION
25°C, pH=12.2 WITH KOH
SONICS, 2.75 KHz
POWER LEVEL 6
CONTROL
% TRANSMITTANCE
TIME, MINUTES
100
90
80
70
60
50
0
20
40
60
80
100
120
140
160
180
200
220
240
260

FIG. 3

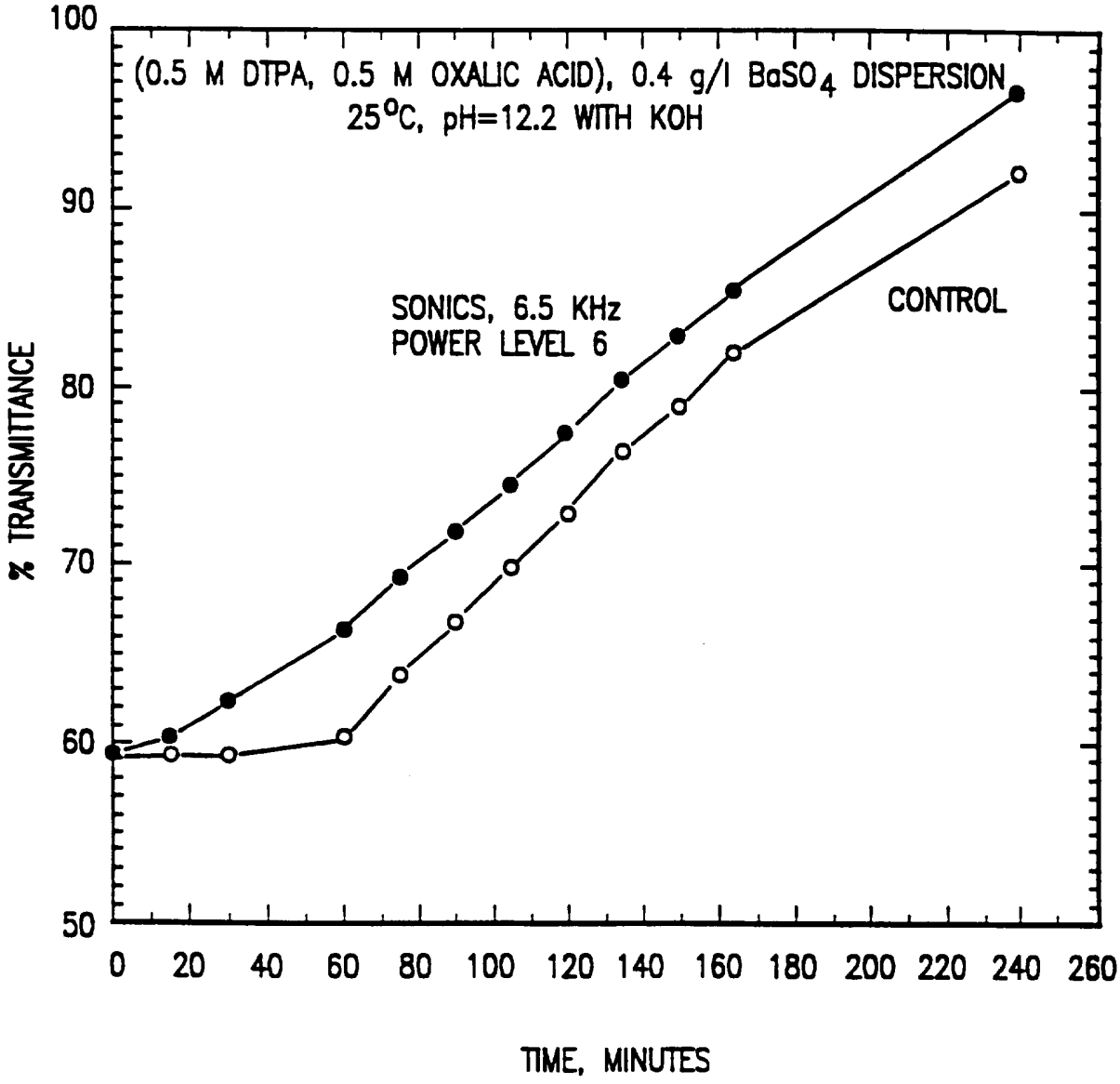

(0.5 M DTPA, 0.5 M OXALIC ACID), 0.4 g/l $BaSO_4$ DISPERSION
25°C, pH=12.2 WITH KOH
SONICS, 6.5 KHz
POWER LEVEL 6
CONTROL
% TRANSMITTANCE
TIME, MINUTES
100
90
80
70
60
50
0
20
40
60
80
100
120
140
160
180
200
220
240
260

FIG. 4

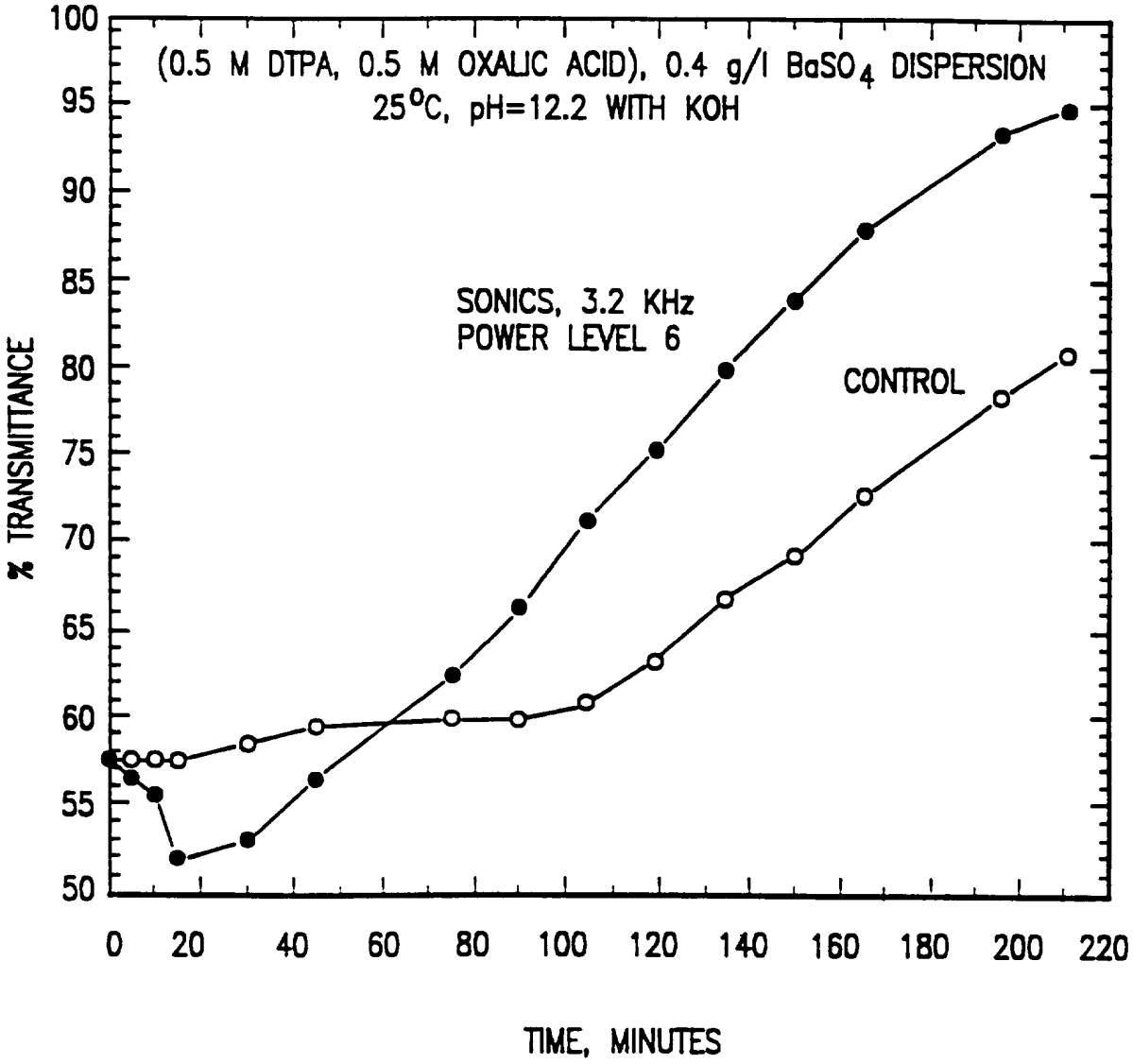

(0.5 M DTPA, 0.5 M OXALIC ACID), 0.4 g/l BaSO4 DISPERSION
25°C, pH=12.2 WITH KOH
SONICS, 3.2 KHz
POWER LEVEL 6
CONTROL
% TRANSMITTANCE
TIME, MINUTES
100
95
90
85
80
75
70
65
60
55
50
0
20
40
60
80
100
120
140
160
180
200
220

FIG. 5

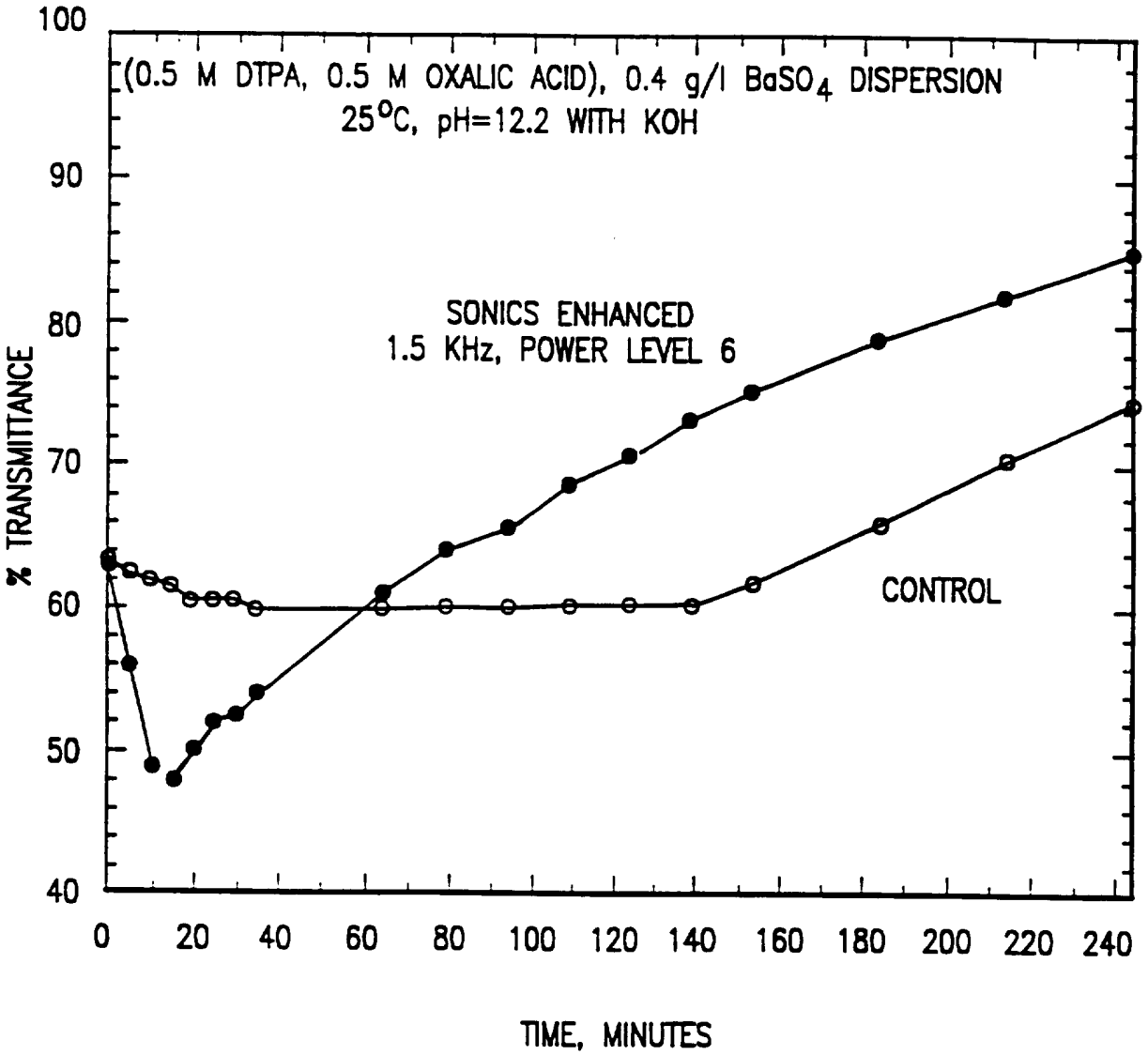

(0.5 M DTPA, 0.5 M OXALIC ACID), 0.4 g/l BaSO4 DISPERSION
25°C, pH=12.2 WITH KOH
SONICS ENHANCED
1.5 KHz, POWER LEVEL 6
CONTROL
% TRANSMITTANCE
TIME, MINUTES
100
90
80
70
60
50
40
0
20
40
60
80
100
120
140
160
180
200
220
240

FIG. 6

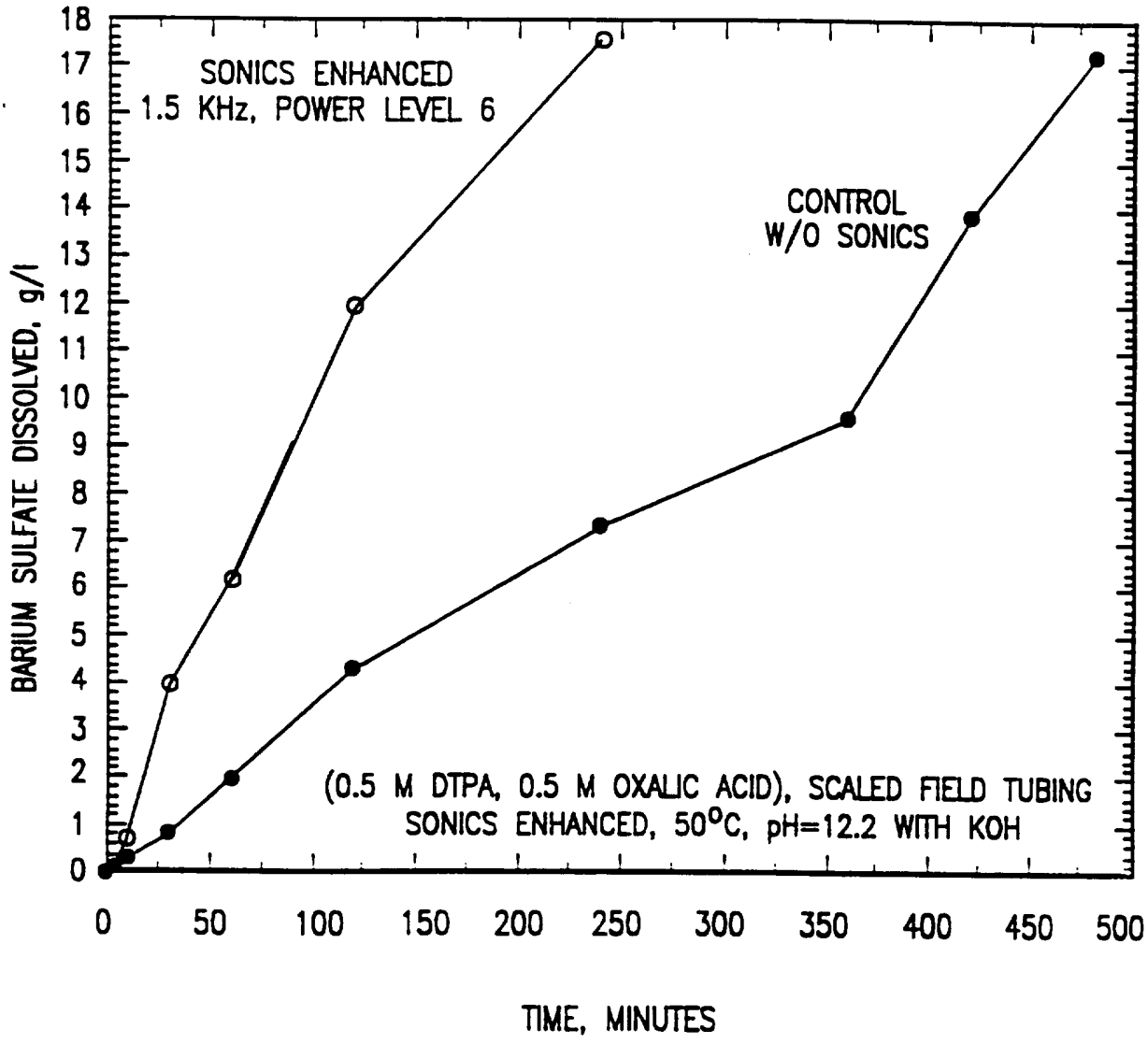

SONICS ENHANCED
1.5 KHz, POWER LEVEL 6
CONTROL
W/O SONICS
(0.5 M DTPA, 0.5 M OXALIC ACID), SCALED FIELD TUBING
SONICS ENHANCED, 50°C, pH=12.2 WITH KOH
BARIUM SULFATE DISSOLVED, g/l
TIME, MINUTES
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
0
50
100
150
200
250
300
350
400
450
500

FIG. 7

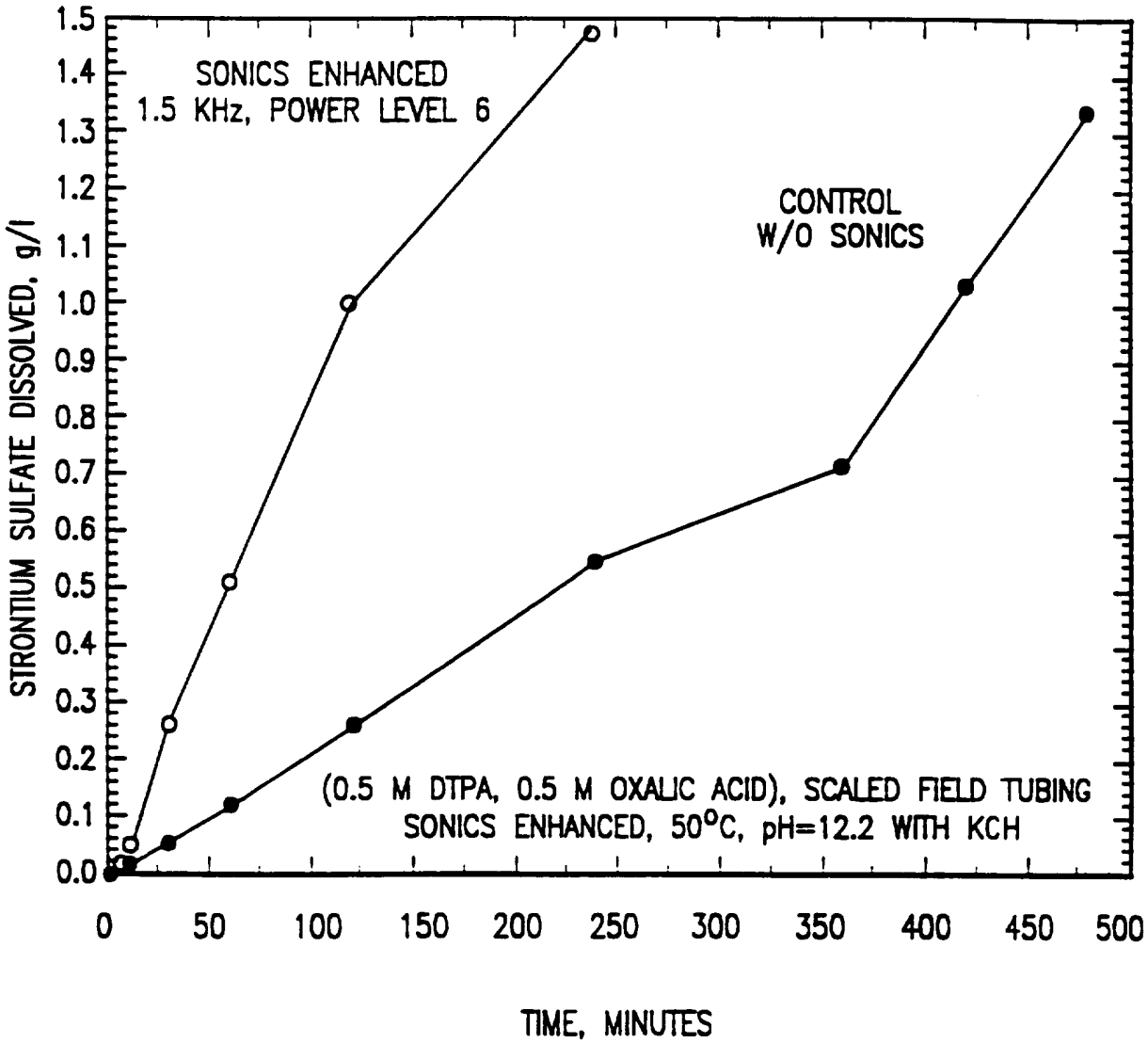

SONICS ENHANCED
1.5 KHz, POWER LEVEL 6
CONTROL
W/O SONICS
(0.5 M DTPA, 0.5 M OXALIC ACID), SCALED FIELD TUBING
SONICS ENHANCED, 50°C, pH=12.2 WITH KCH
STRONTIUM SULFATE DISSOLVED, g/l
TIME, MINUTES
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
0
50
100
150
200
250
300
350
400
450
500

FIG. 8

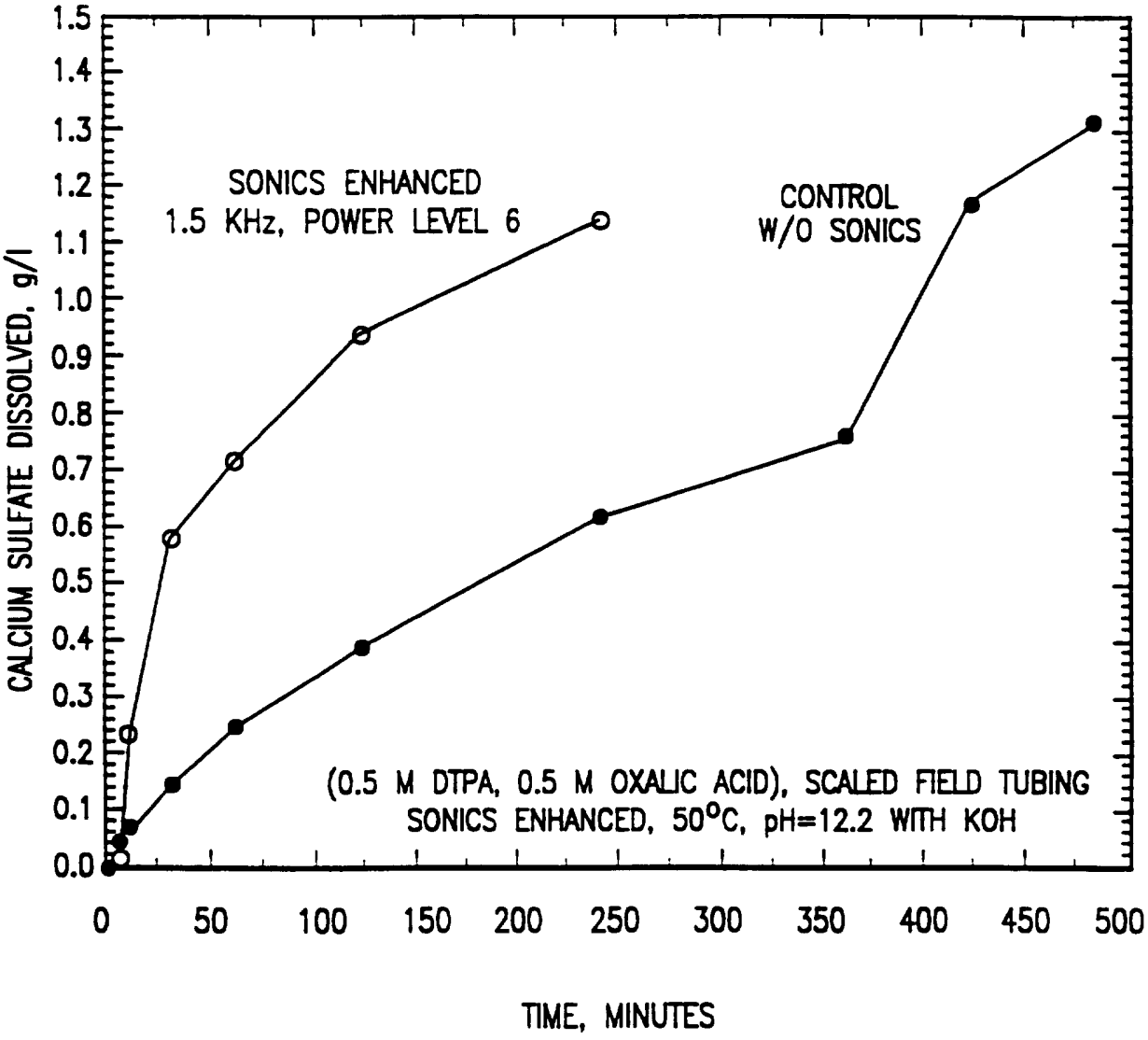

SONICS ENHANCED
1.5 KHz, POWER LEVEL 6
CONTROL
W/O SONICS
(0.5 M DTPA, 0.5 M OXALIC ACID), SCALED FIELD TUBING
SONICS ENHANCED, 50°C, pH=12.2 WITH KOH
CALCIUM SULFATE DISSOLVED, g/l
TIME, MINUTES
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
0
50
100
150
200
250
300
350
400
450
500

FIG. 9

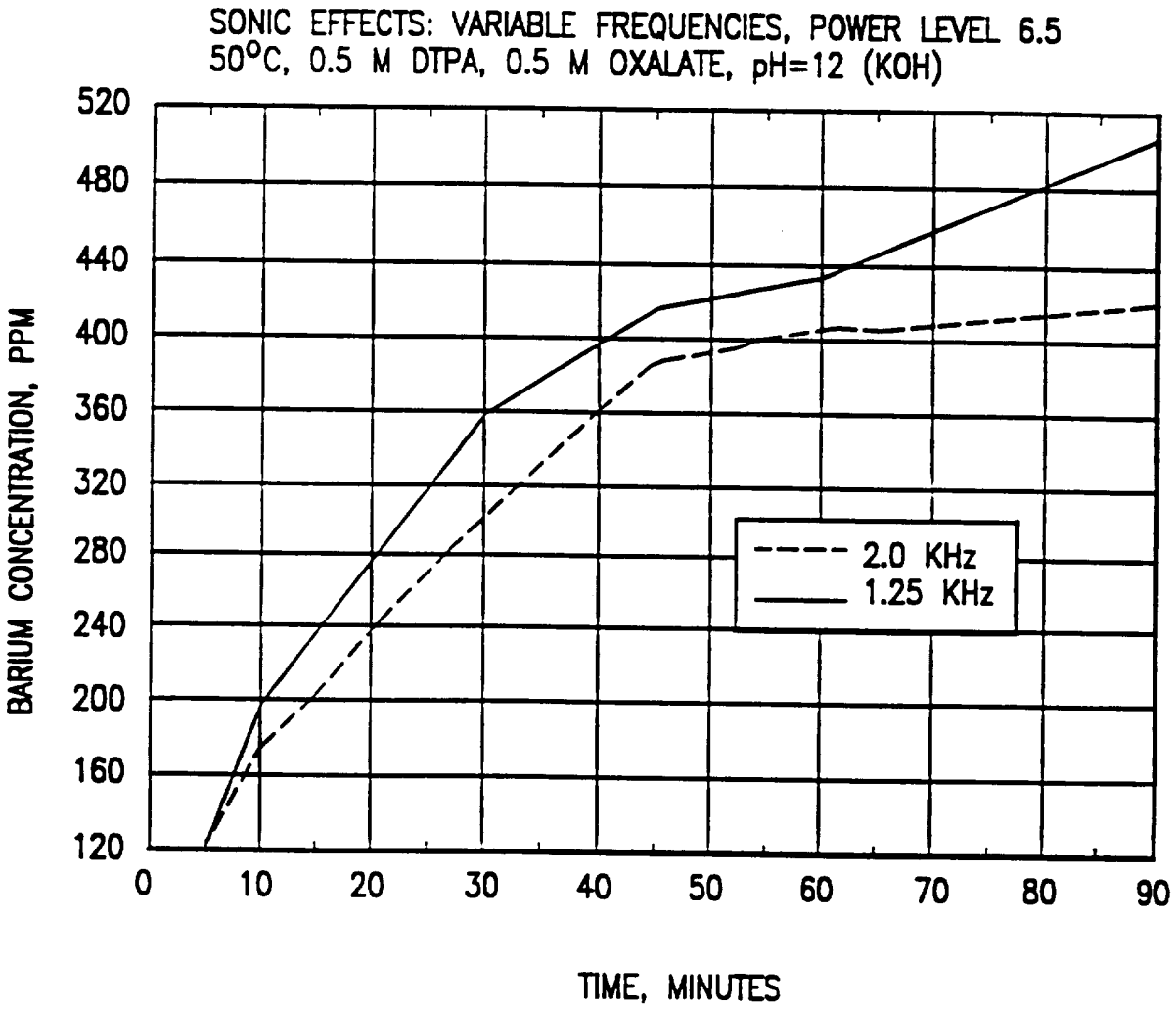
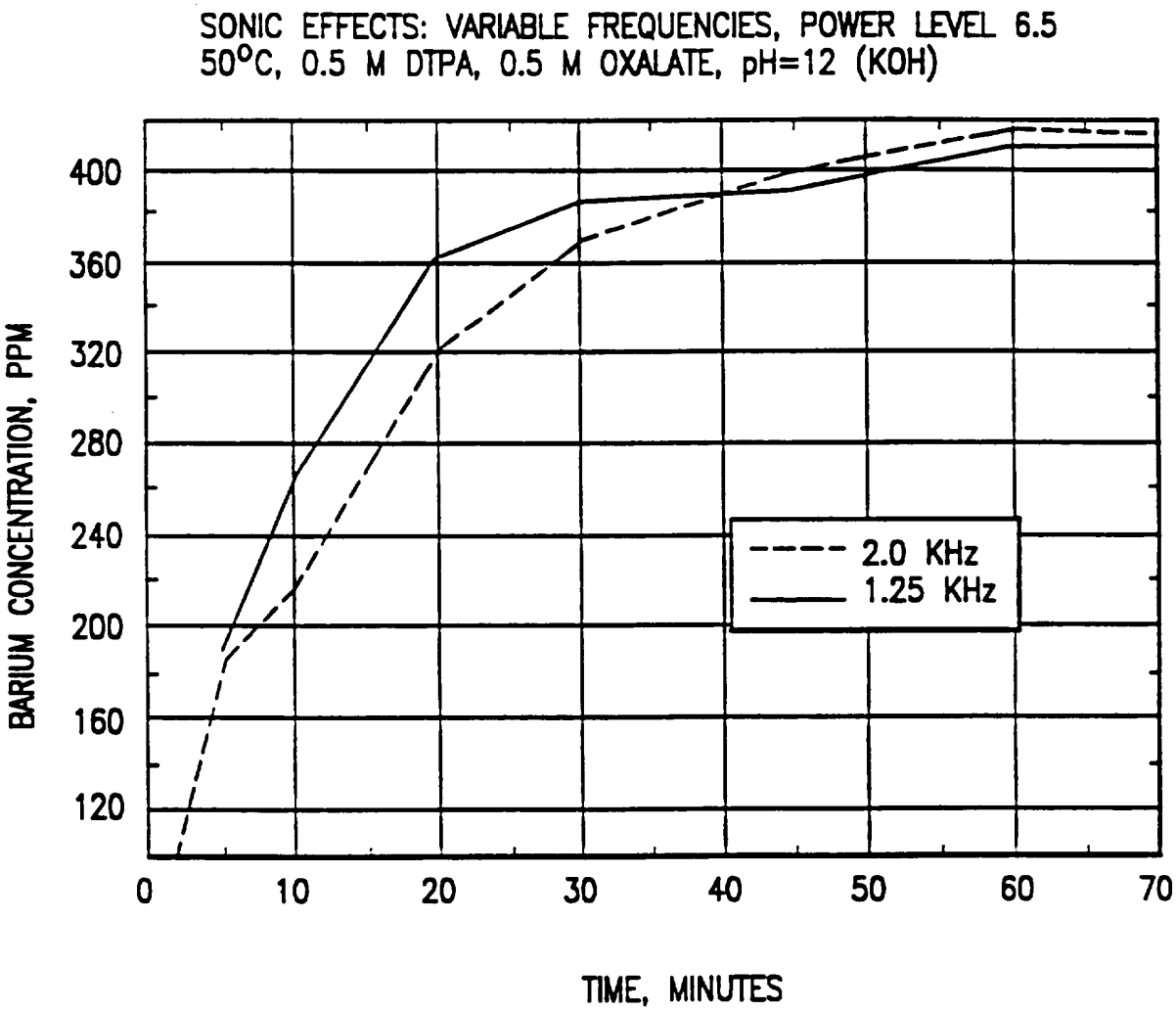

SONIC EFFECTS: VARIABLE FREQUENCIES, POWER LEVEL 6.5
50°C, 0.5 M DTPA, 0.5 M OXALATE, pH=12 (KOH)
BARIUM CONCENTRATION, PPM
520
480
440
400
360
320
280
240
200
160
120
0
10
20
30
40
50
60
70
80
90
TIME, MINUTES
2.0 KHz
1.25 KHz

FIG. 10


SONIC EFFECTS: VARIABLE FREQUENCIES, POWER LEVEL 6.5
50°C, 0.5 M DTPA, 0.5 M OXALATE, pH=12 (KOH)
BARIUM CONCENTRATION, PPM
400
360
320
280
240
200
160
120
0
10
20
30
40
50
60
70
TIME, MINUTES
2.0 KHz
1.25 KHz

INTERNATIONAL SEARCH REPORT

In..national application No.
PCT/US95/09239

A. CLASSIEICATION OF SUBJECT MATTER
IPC(6) :C22B 26/20; B08B 7/00; E21B 37/00
US CL :423/155, 658.5; 134/1; 166/177,311
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCIIED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/155, 658.5; 134/1; 166/177,311

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.
Y	US, A, 4,980,077 (MORRIS ET AL) 25 December 1990, abstract and claims 1 and 12.	1-12
Y	US, A, 4,320,528 (SCHARTON ET AL) 16 March 1982, abstract, col. 3, lines 35-36, col. 5, lines 19-29, col. 8, lines 55-63 and claim 1.	1-12
Y	US, A, 3,648,769 (SAWYER) 14 March 1972, abstract and col. 1, lines 26-40.	1-12
Y	US, A, 4,683,556 (WILLIS) 28 JULY 1987, col. 4, lines 6-14.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"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)

"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

"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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
24 AUGUST 1995	19OCT1995
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 STEVEN BOS Telephone No. (703) 308-2537

Form PCT/ISA/210 (second sheet)(July 1992)★