Title: PROCESS FOR RECOVERING COPPER SULPHIDE FROM COPPER BEARING ORES BY FROTH FLATION

Abstract: Process for recovering copper sulphide and optionally molybdenum sulphide from a copper bearing ore by froth flotation consisting in: - crushing said ore, mixing the obtained ground powder with at least a collector and water, - aerating the slurry, removing and concentrating the mineral froth formed at the surface of the bath, wherein the collector is a thioglycolic acid derivate having the following formula: - R1 is N or O, - R2 is an alkyl group having 2 to 12 carbon atoms.
PROCESS FOR RECOVERING COPPER SULPHIDE FROM COPPER BEARING ORES BY FROTH FLOTATION

The present invention relates to improvements for the selective separation of the copper (Cu) and optionally copper-molybdenum (Cu-Mo) values from copper bearing ores by flotation. More particularly, the present invention relates to a process for such separation using as collector, a thioglycolic acid derivate, optionally in combination with any other collector commonly used in mining processes.

The majority of the world's copper resources are in the form of copper sulphide, in particular chalcopyrite (CuFeS₂) or chalcocite (Cu₂S). A sulphide is a compound in which a metal, such as copper, is bonded to one or more sulphur atoms.

For copper sulphides, froth flotation processes are widely used to separate copper sulphides from the remaining ore materials.

The art of froth flotation to separate and concentrate desired ores from undesirable minerals and gangue is a well-known process. Mineral ore is crushed and slurried with water to approximately 30% solids. Then, it is fed to the grinding mill where mineral collectors and frothers are added. The mineral collectors will adsorb onto the desired mineral's surface and cause the proper amount of hydrophobic characteristics to allow the desired mineral to stick to the frother bubble and be removed from the undesirable gangue material. Optionally, the person skilled in the art can add depressants to the flotation cell to further remove by settling undesirable species having tendency to stick to the frother bubbles such as iron. The ore/water slurry is then dosed with a given amount of frother on its way to the froth flotation cells. Air is blown up through the bottom of the flotation cell while an agitator keeps the heavy slurry well distributed. The air bubbles along with the frother create a mineral froth that is skimmed off the flotation cell, concentrated and further processed.
Typically, copper deposits contain other types of minerals associated with the copper sulphides. Molybdenite, for example, is a naturally occurring molybdenum sulphide (MoS$_2$) which is mainly recovered as a by-product in the refining of copper ores by froth flotation. Copper deposits also frequently contain significant amount of iron sulphide, which is an undesirable element in the final concentrate due to its deleterious effect to the equipment used for the reduction of copper sulphide ores to copper.

The economic performance of copper mineral is therefore directly linked with the effectiveness and selectiveness of the flotation process used. Accordingly, there is a constant need to provide improved froth flotation process that will allow the recovery of increased amount of highly pure valuable minerals from ores containing copper (i.e.: copper sulphide and optionally molybdenite).

The present invention relates to improved ore flotation processes. More specifically, the present invention relates to a novel collector material in froth flotation circuits to facilitate increased recovery of copper ore and optionally molybdenum values with improved suppression of deleterious contaminants such as iron sulphide. More particularly, the present invention relates to a process for such recovery using as collector, in whole or in part, a thioglycolic acid derivate, optionally in combination with another common collector. The secondary collector can be dosed as a single homogeneous blend with the thioglycolic acid derivate or in two distinct points or as an heterogeneous formulations. Optionally, the mix of collectors as described hereinabove can efficiently be formulated with any other common froth flotation cell reagents such as frother, depressant, solvent, and emulsifier.

Most copper sulphide ores are concentrated using the froth flotation process.

Froth flotation is achieved when copper sulphide and optionally molybdenum sulphides particles are separated from other particles based on their surface potential.
For this, ground powdered ore is mixed with chemicals and water to form a slurry (or pulp). The chemicals used, known as collectors, are reagents containing both a nonpolar group (hydrocarbon radical) and a polar group (hydrophilic) so as the hydrophilic group can react with the copper sulphides and optionally molybdenum sulphides mineral to make it hydrophobic on its surface. The corresponding slurry is then aerated. The hydrophobic copper (Cu) or copper-molybdenum (Cu-Mo) bearing ore particles escape the water by attaching to the air bubbles, which rise to the bath surface forming a foam, called froth. After that, the froth is removed as a concentrate to be treated whereas the residue (hydrophilic particles) is discharged with the tailings stream.

Collectors commonly used for copper containing ores are xanthates, xanthate esters, xanthate formates, dithiocarbamates, phosphinates, dithiophosphates and thionocarbamates. However, for some cases the recovery and in particular the selectivity achieved are not satisfactory especially with regard to ores having high contents of iron sulphide.

It is an object of this invention to provide an improvement in the process of recovering copper and, if any, also molybdenum values from a copper-bearing ore by froth flotation which comprises using as collector, in whole or in part, thioglycolic acid derivate, optionally in combination with another common collector.

Surprisingly, it has been found that the use of thioglycolic acid derivate(s) as unique collector or in combination with another common one dramatically improves the selective separation of copper (Cu) or copper-molybdenum (Cu-Mo) bearing ore especially in the case when there is high content of iron sulphide minerals in the pulp.

As a consequence the invention concerns a process for recovering copper sulphide and optionally molybdenum sulphide from a copper bearing ore by froth flotation consisting in:

- crushing said ore,
- mixing the obtained ground powder with at least a collector and water,
- aerating the slurry,
- removing and concentrating the mineral froth formed at the surface of the bath,

wherein the collector is a thioglycolic acid derivate having the following formula:

\[
\text{HS} - \text{CH}_2 - \text{C} - \text{R}_1 - \text{R}_2
\]

- \( \text{R}_1 \) represents \( \text{N} \) or \( \text{O} \),
- \( \text{R}_2 \) represents an alkyl group having 2 to 12 carbon atoms.

In a preferred embodiment, the collector is an alkyl thioglycolate. In that case \( \text{R}_1 \) represents an oxygen atom.

Whatever \( \text{R}_1 \), \( \text{R}_2 \) represents a linear alkyl chain, a branched alkyl, an aryl alkyl, an ethoxylated alkyl all of them having advantageously 2 to 12 carbon atoms, more advantageously having 6 to 10 carbon atoms, or any modified alkyl group having 2 to 12 carbon atoms, advantageously having 6 to 10 carbon atoms.

For example, the collector of the invention is chosen from the group containing n-butyl thioglycolate, n-hexyl thioglycolate, n-octyl thioglycolate, 2-ethylhexyl thioglycolate or n-dodecyl thioglycolate.

In a preferred embodiment, the alkyl thioglycolate has a linear or branched alkyl group consisting of 8 carbon atoms. It is named octyl thioglycolate.

Thioglycolic acid derivate(s) of the invention may be used alone or as a mixture of two or more of them.

A preferred non limited process of manufacturing Thioglycolic acid derivate(s) of the invention is described as follow: thioglycolic acid is mixed with the desired substituted primary or secondary alcohol or N-substituted amine, depending on the nature of the desired thioglycolic acid derivate. Heat is applied as needed and
optionally an acid catalyst such as sulphuric acid, methane sulfonic acid, para toluene sulfonylic acid, a sulfonated resin can be added to enhance reaction rate. The water formed by product is removed by distillation continuously and thus all the thioglycolic acid is converted to the corresponding thioglycolic acid derivate.

The process of the invention can require in addition to the thioglycolic acid derivate, at least a second collector which is chosen from groups consisting of di-alkyl thionocarbamates, di-alkyl xanthogen formates, di-alkyl xanthogen esters, di-alkyl dithiophosphates, di-alkyl monothiophosphates, di-alkyl dithiocarbamates, phosphinates, or any of the xanthates.

The composition of the new collector involves 5 to 100% by weight of any C₂ through C₁₂ thioglycolic acid derivate, preferably 5 to 75%, the rest to 100% by weight consisting of at least one of the common mining collectors having C-S bond, a P-S bond, or an S=C-N bond such as collectors chosen from groups containing di-alkyl thionocarbamates, di-alkyl dithiocarbamates, phosphinates, di-alkyl xanthogen formates, di-alkyl xanthogen esters, di-alkyl dithiophosphates, di-alkyl monothiophosphates, or any of the xanthates. Thioglycolic acid derivate(s) of the invention work with all mining collectors which can be used alone or in combination.

Optionally, the mix of collectors as described above can efficiently be formulated with any common flotation cell reagents such as but not limited to depressants, frothers, emulsifiers, solvents in any suitable ratio.

When used in combination with another common collector, in some cases, the thioglycolic acid derivate will not solubilize in it so it must be dosed as a secondary collector in some fashion to maintain the ratios stated above, up to and including 3 parts thioglycolic acid derivate to 1 part common collector. To the opposite, when the thioglycolic acid derivate can solubilise, the compositions of the present invention eliminate the need for separate additions, thus reducing the number of processing steps.
The thioglycolic acid derivate containing collectors composition showed a strong and favorable effect on high pyrite copper ores. The iron recovery in the bulk copper float was cut by 20 to 42%. The rejection of iron in the flotation cell equates to sizeable increases in the grade assays for copper and/or molybdenum in the concentrate.

Generally, the thioglycolic acid derivate is used in an amount varying from about 0.001 to about 0.1 kg of collector per ton of ore, preferably about 0.005 to about 0.05 kg per ton. Depending upon the particular copper ore processed, the optimum dosage can easily be determined by trial.

**Standard Blasthole Float:**

A standard lab froth flotation procedure has been applied for the evaluation of the performance of the various derivates of thioglycolates and as well as a couple of formulated collectors:

**A-Materials and Equipment**

1500 g sample / test run, 100% -10 mesh, 1500 ml mill water, Reagents : collectors depressants and frothers, Lime as needed, Make-up mill water, Large ball mill with grinding media (balls), Rolls connected to timer, Strainer and bucket, Denver float machine (small impeller), Minnovex MFT float cell 4.6 liter, Denver 750 ml float cell, Filter and filter paper, pH meter which has been calibrated prior to floating, micro liter syringes, Siphon hose and 600 ml beaker, Sample pans, drying oven

**B-Procedure**

Place 1500 g sample, 1500 ml mill water, and estimated amount of lime to bring pH to 9.0 in ball mill. Fasten lid and place on rolls for 10 min. After grinding, dump sample and balls through strainer into bucket to remove balls. Carefully wash sample from ball mill, balls, and strainer into bucket using mill water. Pour sample from
bucket into 4.6 liter cell. Add enough mill water to bring level up to line. Weigh cell and record on float sheet. Place cell on float machine. Lower the impeller into cell and adjust the rpm to 1200. Turn on machine making sure that the air is shut off. Place pH probe into cell. Record the pH. Add lime to bring pH up to desired value (10.5). Record this pH. Remove pH probe. Add collectors, depressants and frothers. Give the sample two minutes conditioning time. Turn on air. Float sample for 15 minutes pulling concentrate from top of cell every 15 seconds. Rinse down sides as needed. Turn off air. Place pH probe in cell and record ending pH. Syphon 600 ml of tail slurry into beaker. Wet screen material through a 400 mesh screen. Ro tap the oversize material using 65, 150, and 400 mesh screens. Weigh each fraction and assay for Cu and Fe. Reduce rpm of machine to 900. Turn off agitator, raise impeller, wash any residue from impeller and sides of cell. Remove cell and rinse into a 4 liter beaker. Floe the slurry and filter when it has settled. Put rougher con into 750 ml cell. Place cell on float machine and lower impeller into cell. Put pH probe into cell. Record pH. Add lime to increase pH to 11.5. Record pH and grams of lime used. Remove probe. Turn on air and float for 5 min. Rinse sides as needed with mill water. Turn off the air. Place pH probe in cell and record pH. Turn off agitator, raise impeller, wash any residue from impeller and sides of cell. Remove cell from machine. Filter and dry samples for assay. Assay for T Cu, T Fe, Cu(SO4), Mo, and insol on the concentrate and cleaner tail.

Reference is now made to the following non-limiting examples.

Example 1 - Ore designation: Chalcocite (CuS), Chalcopyrite (CuFeS2), Pyrite (FeS). Quartz

<table>
<thead>
<tr>
<th>Collector @ 19 grams per ton of ore</th>
<th>Cu Recovery</th>
<th>Fe Recovery</th>
<th>Cu Grade Assay</th>
<th>Fe Grade Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% Diisobutyl dithiophosphate / 20% Diisobutyl monothiophosphate blend</td>
<td>89.4</td>
<td>6.6</td>
<td>7.63</td>
<td>13.3</td>
</tr>
<tr>
<td>40% Diisobutyl dithiophosphate / 10% Diisobutyl monothiophosphate / 50% Octyl thioglycolate blend</td>
<td>89.4</td>
<td>3.8</td>
<td>10.32</td>
<td>10.44</td>
</tr>
</tbody>
</table>
From above example, one can illustrate the positive effect of octyl thioglycolate addition to DTP and MTP on purity of floated copper by improving selectivity to iron at both dosages.

Example 2 - Ore designation: Chalcocite (CuS), Chalcopyrite (CuFeS), Pyrite (FeS).

<table>
<thead>
<tr>
<th>Collector @ 24 grams per ton of ore</th>
<th>Cu Recovery</th>
<th>Fe Recovery</th>
<th>Cu Grade Assay</th>
<th>Fe Grade Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% Diisobutyl dithiophosphate / 20% Diisobutyl monothiophosphate blend</td>
<td>89.8</td>
<td>6.9</td>
<td>7.44</td>
<td>13.59</td>
</tr>
<tr>
<td>40% Diisobutyl dithiophosphate / 10% Diisobutyl monothiophosphate / 50% Octyl thioglycolate blend</td>
<td>89.7</td>
<td>3.7</td>
<td>10.51</td>
<td>10.38</td>
</tr>
</tbody>
</table>

From above example, one can illustrate the positive effect of octyl thioglycolate addition to DTP and MTP on purity of floated copper by improving selectivity to iron at both dosages.

<table>
<thead>
<tr>
<th>Formulated collector @ 26 grams per ton of ore</th>
<th>Cu Recovery</th>
<th>Fe Recovery</th>
<th>Cu Grade Assay</th>
<th>Fe Grade Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Isopropylethyl thionocarbamate</td>
<td>78.2</td>
<td>38.3</td>
<td>8.81</td>
<td>20.78</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% Octyl thioglycolate blend</td>
<td>78.3</td>
<td>29.4</td>
<td>12.09</td>
<td>19.34</td>
</tr>
<tr>
<td>35% Isopropylethyl thionocarbamate / 55% Octyl thioglycolate blend / 10% Methyl isobutyl carbinol</td>
<td>78</td>
<td>30.21</td>
<td>11.81</td>
<td>19.66</td>
</tr>
<tr>
<td>33% Isopropylethyl thionocarbamate / 52% Octyl thioglycolate blend / 10% Methyl isobutyl carbinol / 5% Sodium hydrosulfide</td>
<td>77.9</td>
<td>29.17</td>
<td>11.49</td>
<td>18.56</td>
</tr>
<tr>
<td>35% Isopropylethyl thionocarbamate / 55% Octyl thioglycolate blend / 10% Methyl isobutyl carbinol</td>
<td>78</td>
<td>30.21</td>
<td>11.81</td>
<td>19.66</td>
</tr>
</tbody>
</table>

From above example, one can illustrate the positive effect of octyl thioglycolate on purity of floated copper for various formulations containing IPETC / OTG including mix with frothers and depressants.
Example 3 - Ore designation: Chalcocite (Cu₇S), Chalcopyrite (CuFeS?), Pyrite (Fe₇S). Galena

<table>
<thead>
<tr>
<th>Collector @ 24 grams per ton of ore</th>
<th>Cu Recovery</th>
<th>Fe Recovery</th>
<th>Mo Recovery</th>
<th>Cu Grade Assay</th>
<th>Fe Grade Assay</th>
<th>Mo Grade Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Sodium isopropyl xanthate</td>
<td>79.6</td>
<td>41</td>
<td>83.4</td>
<td>9.12</td>
<td>21.89</td>
<td>0.341</td>
</tr>
<tr>
<td>25% Sodium isopropyl xanthate / 75% Octyl thioglycolate blend</td>
<td>79.5</td>
<td>27.1</td>
<td>85.1</td>
<td>12.91</td>
<td>18.19</td>
<td>0.59</td>
</tr>
<tr>
<td>50% Sodium isopropyl xanthate / 50% Octyl thioglycolate blend</td>
<td>79.1</td>
<td>28.3</td>
<td>84.5</td>
<td>11.88</td>
<td>18.42</td>
<td>0.518</td>
</tr>
<tr>
<td>75% Sodium isopropyl xanthate / 25% Octyl thioglycolate blend</td>
<td>80.2</td>
<td>34.1</td>
<td>83.9</td>
<td>11.01</td>
<td>20.15</td>
<td>0.468</td>
</tr>
<tr>
<td>6 grams per ton 100% Sodium isopropyl xanthate + 18 grams per ton 100% Octyl thioglycolate (Dosed separately)</td>
<td>79.4</td>
<td>27.2</td>
<td>85</td>
<td>12.88</td>
<td>18.11</td>
<td>0.6</td>
</tr>
</tbody>
</table>

From above example, one can illustrate the positive effect of octyl thioglycolate on purity of floated copper and molybdenum for various formulations containing SIPX/OTG in different ratios added as a blend or in two separates stages.

Example 4 - Ore designation: Chalcocite (Cu₇S), Chalcopyrite (CuFeS?), Pyrite (Fe₇S)

<table>
<thead>
<tr>
<th>Collector @ 24 grams per ton of ore</th>
<th>Cu Recovery</th>
<th>Fe Recovery</th>
<th>Mo Recovery</th>
<th>Cu Grade Assay</th>
<th>Fe Grade Assay</th>
<th>Mo Grade Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Isopropylethyl thionocarbamate</td>
<td>82</td>
<td>49.3</td>
<td>46.7</td>
<td>6.87</td>
<td>22.55</td>
<td>0.336</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% Octyl thioglycolate blend</td>
<td>84.3</td>
<td>37.12</td>
<td>60.49</td>
<td>7.4</td>
<td>17.62</td>
<td>0.479</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% Butyl thioglycolate blend</td>
<td>82.5</td>
<td>38.6</td>
<td>59</td>
<td>7.08</td>
<td>18.3</td>
<td>0.404</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% Allyl thioglycolate blend</td>
<td>84</td>
<td>39.2</td>
<td>59.9</td>
<td>7.32</td>
<td>18.8</td>
<td>0.459</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% Cresyl thioglycolate blend</td>
<td>83.1</td>
<td>38.1</td>
<td>57.8</td>
<td>7.19</td>
<td>18.51</td>
<td>0.4</td>
</tr>
<tr>
<td>40% Isopropylethyl thionocarbamate / 60% 3-mercapto-1(N-octyl)propionamide</td>
<td>83.8</td>
<td>41</td>
<td>56.8</td>
<td>6.81</td>
<td>17.91</td>
<td>0.412</td>
</tr>
</tbody>
</table>

From above example, one can illustrate the positive effect of different substituted thioglycolate on purity of floated copper and molybdenum for various formulations containing IPETC and a substituted thioglycolate.
CLAIMS

1/ Process for recovering copper sulphide and optionally molybdenum sulphide from a copper bearing ore by froth flotation consisting in:

- crushing said ore,
- mixing the obtained ground powder with at least a collector and water,
- aerating the slurry,
- removing and concentrating the mineral froth formed at the surface of the bath,

wherein the collector is a thioglycolic acid derivative having the following formula:

\[ \text{HS} \text{CH}_2 \text{C} \text{-R}_1 \text{-R}_2 \]

- R1 is N or O,
- R2 is an alkyl group having 2 to 12 carbon atoms.

2/ Process according to claim 1, wherein R1 represents an oxygen atom.

3/ Process according to claim 1, wherein R2 represents a linear alkyl chain, a branched alkyl, an aryl alkyl, an ethoxylated alkyl.

4/ Process according to claim 3, wherein R2 has 2 to 12 carbon atoms, advantageously 6 to 10 carbon atoms.

5/ Process according to claim 1, wherein said collector is chosen from the group containing n-butyl thioglycolate, n-hexyl thioglycolate, n-octyl thioglycolate, 2-ethylhexyl thioglycolate or n-dodecyl thioglycolate.

6/ Process according to claim 1, wherein said collector is octyl thioglycolate.
1/ Process according to one of preceding claims wherein the collector contains at least a second collector chosen from groups containing di-alkyl thionocarbamates, di-alkyl xanthogen formates, di-alkyl xanthogen esters, di-alkyl dithiophosphates, di-alkyl monothiophosphates, di-alkyl dithiocarbamates, phosphinates, or any of the xanthates.

8/ Process according to claim 1, wherein the collector contains 5 to 75% of a thioglycolic acid derivate, the rest to 100% by weight consisting of at least a second collector which is chosen from groups containing di-alkyl thionocarbamates, di-alkyl xanthogen formates, di-alkyl xanthogen esters, di-alkyl dithiocarbamates, phosphinates, di-alkyl dithiophosphates, di-alkyl monothiophosphates, or any of the xanthates.

9/ Process according to claim 8, wherein the ratio thioglycolic acid derivate/second collector is up to and includes 3/1.

10/ Process according to claim 1, wherein the mix of collectors is further formulated with other froth flotation reagents consisting of depressants, frothers, emulsifiers, solvents.

11/ Process according to claim 1, wherein the thioglycolic acid derivate is used in an amount varying from about 0.001 to about 0.1 kg of collector per ton of ore, preferably about 0.005 to about 0.05 kg per ton.
INTERNATIONAL SEARCH REPORT

PCT/IB2008/050844

A CLASSIFICATION OF SUBJECT MATTER

INV. B03D1/012 B03D1/004 B03D1/02

B FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B03D B03B C22B COIG

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical search terms used)

C DOCUMENTS CONSIDERED TO BE RELEVANT

Category Clation of document with indication where appropriate of the relevant passages Relevant to claim No

Y US 3 570 772 A (BOOTH ROBERT BEN ET AL) 16 March 1971 (1971-03-16) column 1, line 11 - line 48, claims 1-7; examples 1-12 column 8, line 8 - line 57 1-6,10, 7-9

A US 3 235 077 A (EVERETT MCGARRY PHILLIP ET AL) 15 February 1966 (1966-02-15) column 1, line 9 - line 27; claims 1-8,11,12; examples 1,2, tables 1,2 column 1, line 50 - line 65 column 2, line 31 - line 34 1-6,10, 11

A US 4 293 406 A (WERNEKE MICHAEL F ET AL) 6 October 1981 (1981-10-06) the whole document 1-6,10, -/-

X Further documents are listed in the continuation of Box C

X 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 but 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 invention 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

'S' document member of the same patent family

Date of the actual completion of the international search 28 November 2008

Date of mailing of the international search report 08/12/2008

Name and mailing address of the ISA/

European Patent Office

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Authorized officer

de La Morinerie, B
<table>
<thead>
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<th>Category</th>
<th>Citation or document with indication where appropriate of the relevant passages</th>
<th>Relevant to claim No</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>US 2 919 025 A (BEN BOOTH ROBERT ET AL) 29 December 1959 (1959-12-29) claims 1,5,9-12; example 11</td>
<td>7</td>
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<tr>
<td>A</td>
<td>US 4 139 455 A (GRIFFITH ROBERT M ET AL) 13 February 1979 (1979-02-13) column 6, line 60 - column 7, line 20; claims 1,6,7; examples 1,2</td>
<td>7,8,10</td>
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<tr>
<td>A</td>
<td>US 4 040 950 A (ZIPPERIAN DONALD EDWIN ET AL) 9 August 1977 (1977-08-09) column 6; claims 1-5; examples 42-46</td>
<td>7</td>
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<tr>
<td>A</td>
<td>US 2 449 984 A (GIBBS HAROLD L) 28 September 1948 (1948-09-28) column 6, line 3 - line 7; claims 14,16-18,20,22,23; figure 1</td>
<td>1,7,10</td>
</tr>
<tr>
<td>A</td>
<td>US 4 532 031 A (WANG SAMUEL S [US] ET AL) 30 July 1985 (1985-07-30) claims 1-4; example 5; tables I,III-V</td>
<td>1,7,10</td>
</tr>
</tbody>
</table>
Continuation of Box II.2

Claims Nos.:

The collector, thioglycolic acid derivate, the formula of which is mentioned in claim 1 and page 4 of the description is not clearly defined when R1 is N, because the second substituent of N is not specified, and it not specified anywhere in the description. It is not possible to determine to which amide derivate of the thioglycolic acid, claim 1 relates, thus this is not in compliance with the clarity requirement of Article 6 PCT. The search was performed taking into consideration the non-compliance in determining the extent of the search (PCT Guidelines, 9.36 and 9.37).

The extent of the search was consequently limited to the clearly defined part of claim 1: R1 is O; R1 being N has been discarded.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.
**INTERNATIONAL SEARCH REPORT**

**Box No. II** Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. _ I claims Nos.:
   - because they relate to subject matter not required to be searched by this Authority, namely

2. _ I claims Nos/:
   - 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
   - see FURTHER INFORMATION sheet PCT/ISA/210

3 _ I 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 No. III** Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. _ I As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. _ I As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of additional fees.

3. _ I 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.: No.

4. _ I 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**

- _ I The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- _ I The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- _ I No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (April 2005)
# INTERNATIONAL SEARCH REPORT

## Information on patent family members

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