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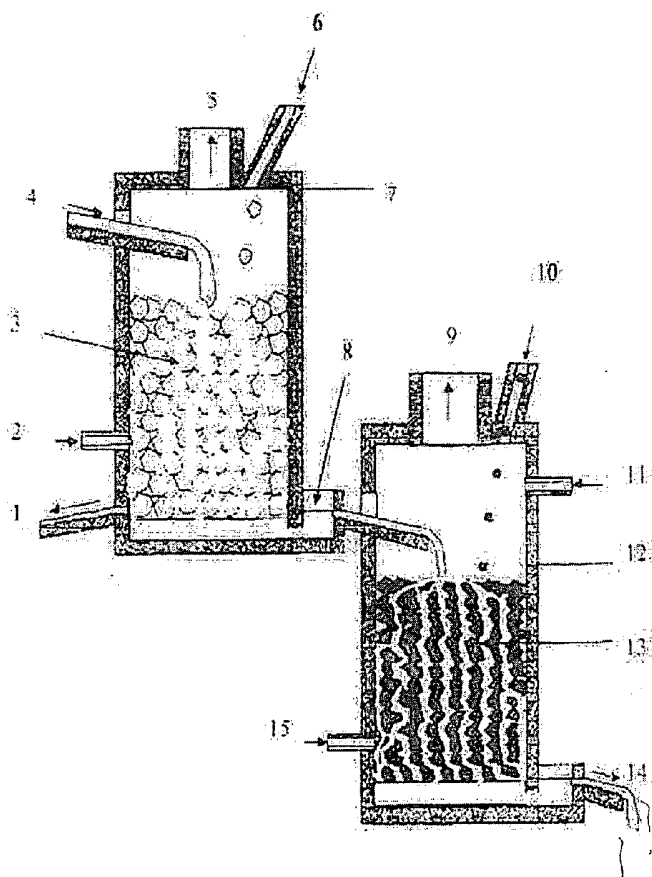
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[Continued on next page]

(54) Title: INSTALLATION FOR CONTINUOUS FIRE REFINING OF COPPER



(57) Abstract: An installation for continuous copper fire refining, said system comprising the components: launder (4) transferring liquid blister copper from continuous converting furnace or from retention furnace into a first oxidation reactor; copper oxidation reactor (7); optionally settler separating oxidized copper and slag; launder (8) transferring oxidized copper from oxidation reactor into reduction reactor; copper reduction reactor (12); and launder (14) transferring reduced copper from reduction reactor to casting will or to retention-casting furnace.



(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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INSTALLATION FOR CONTINUOUS FIRE REFINING OF COPPER

BACKGROUND OF INVENTION

5 1. Field of Invention:

This invention relates to an apparatus for continuous fire refining of blister copper or secondary copper.

10 2. Description of the Prior Art:

Smelting of copper concentrates produces matte and slag. Copper matte is converted into blister copper in Peirce-Smith, Hoboken converters or continuous converting processes such as Kennecott-Outokumpu or Mitsubishi. Blister copper is directed to fire refining process prior electrorefining.

Fire refining of blister copper is carried out in stationary reverberatory or vascular furnaces, called anode furnaces due to the most common casting of refined copper in the form of anodes, which are transferred to electrolytical refining.

Fire refining process is a classical batch process consisting of four stages: charging, oxidation and impurities slagging, reduction and anode casting. Time of refining cycle without the stage of melting varies from 6 to 14 hours.

Oxidized copper after oxidation stage contains from 5000 to 10000 ppm of oxygen. The copper is reduced by carboneous or amonia reductant. The most common reductant in use are the oil or natural gas. The oil or natural gas are injected with air into the bath of molten copper through a tuyere or tuyeres. Copper reduction faces significant limitations in the process rate and efficiency of reductant utilisation. Reduction stage of the liquid copper charge, which fluctuates from 150 to 400 t, varies in the range from 1.2 to 2.0 hours. Reported reductant efficiency is below 50%. Injection of liquid or gaseous reductant into the copper produces black fumes in off-gas due to thermal decomposition of hydrocarbons. Partial carbon utilisation in oxygen reduction from copper causes the presence of carbon particles in the reduction gases, which are partly combusted if the burner flame is oxidising.

Carbon particles are transferred to the furnace off-gas, creating black fumes emitted through a chimney to the atmosphere.

Reduction of a liquid oxidised copper is practised for centuries and it was first described by Georgious Agrícola (G:Agricola: "De Re Metallica", translated from latin, 1^a edition 1556 por Hebert C. Hoover y Lou H. Hoover, Dover Publications, 1950, 535-536). After copper oxidation with air in open hearth furnace and removal of impurities, the copper was reduced with a wood.. Copper reduction with wood (poling) is still practised in some smelters.

L.Klein presented a new idea of the use of gas reductant as a substitute of a wood. ("Gaseous reduction of oxygen-containing copper", J. of Metals, Vol 13, N°8, August 1961, 545-547 ; U.S. Patent N° 2.989.397, June 1961). The study showed that the injection of natural gas with air states a better solution than the injection of only natural gas into a liquid copper. Method of deoxidization of copper with reformed natural gas and related apparatus have been patented by Phelps Dodge Corporation in USA and Canada. (C.Kuzell, M. Fowler, S. Davis y L. Klein: "Apparatus for reforming gases" U.S. Patent N° 3.071.454, January 1963; "Gaseous reduction of oxygen containing copper", Canadian Patent N° 668.598, August 1963)

R. Nenysh, F. Kadler and V. Sedlacek replaced the conventional reduction with wood by ammonia, what allowed for production of high quality copper. Ammonia consumption is about 1 kg/t of copper , when oxygen is reduced from 4000 a 1000 ppm. (R. Henych et al., "Copper refining by gaseous ammonia", J. of Metals, Vol 17, N°4, April 1955).

N. Themelis and P.Schmidt have patented the deoxidisation of a liquid copper by injection of various reformed hydrocarbons (methane, ethane, butane) with steam, leading to the formation of the gas containing carbon monoxide and hydrogen. Patented installation was based on vascular furnace. ("Apparatus and process for the gaseous deoxidisation of molten metal, Canadian Patent N° 827.066, November 1969).

R.Beck, C.Andersen and M. Messner have patented the process of copper deoxidisation with the mix of natural gas/air. ("Process for deoxidising copper with natural gas-air mixture, U.S. Patent N° 3.619.177, November 1971).

Anaconda Company patented a process of copper deoxidisation in vascular furnace by injection through lances of the mix of natural gas or Diesel oil and water vapour (W. Foard and R. Lear: "Refining copper" U.S. Patent N°3,529.956, September, 1970).

J. Henderson and W. Johnson have patented for ASARCO the method of copper reduction in a vascular furnace by natural gas injection through tuyeres ("Gas poling of copper",
5 U.S. Patent N° 3.623.863, November 1971).

G. Mckerrow and D. Panell reviewed in a paper "Gaseous deoxidization of anode copper at the Noranda smelter" Canadian Metallurgical Quarterly, Vol 11, N°4, 1972, 629-633, the evolution of methods of copper deoxidization in Noranda smelter using natural gas injected
10 through tuyeres in a vascular furnace. J. Oudiz made a general review of copper reduction processes ("Poling processes for copper refining", J. of Metals, Vol 25, December 1973, 35-38). Based on industrial data the consumption of reductant, benefits and problems related with the use of various reductants, reforming reactions and reductant efficiency have been analyzed.

L. Lavrov ("Deoxidization of anode copper by natural gas and steam mixture", The Soviet
15 Journal of Non-Ferrous Metals, Vol N°19, N°5, English translation, May 1978, 25-26) verified the use of a mix of natural gas and steam injected through a lance.

C. Toro and V. Paredes ("Sustitución parcial del petróleo diesel por Enap-6 como agente reductor en el proceso de obtención de cobre anódico en la fundición Potrerillos", 34^a
20 Convención Anual IIMCh, Noviembre 1983, Rancagua) developed in industrial scale and demonstrated the possibilities of the use of heavy oil (ENAP-6), with higher sulphur content and lower price, in copper reduction.

J. Minoura ("Bunker fuel oil poling in anode furnace at Kosaka smelter", 114th AIME Annual Meeting, 1985, NY, USA) describes the copper reduction with heavy oil (Bunker
25 C), showing the advantages and lower costs with comparison of copper reduction with ammonia practiced since 1967.

Referencies related to the use of porous plugs in copper fire refining are fragmentary since 1980 decade (P. Goyal, N. Themelis and W. Zanchuk, "Gaseous refining of anode copper",
30 J. of Metals, Vol 34, December 1982, 22-28; P. Goyal, S. Joshi and J. Wang "Porous plug injection in anode refining furnace", J. of Metals, Vol 35, December 1983, 52-58). The

porous plugs use was transferred from iron metallurgy and developed next in the area of metal casting. Industrial applications in copper refining were oriented first to copper desulphurisation by nitrogen stirring. The idea of copper reduction with hydrogen introduced via porous plugs was investigated only in laboratory scale.

- 5 Description of industrial operation of porous plugs is presented in a paper of A. Rigby y M. Lanyi: "Porous plug in molten copper production and refining", CIM'96, August 1996, 393-403.

10 Operational practice and proposed methods of injection, bath agitation and type of reductant, point out the existing problems in oxygen removal from a liquid copper, such as long reduction time, low reductant efficiency and emission of the gases with non-combusted particles.

SUMMARY OF INVENTION

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It is an object of invention to provide a new method of continuous copper fire refining. This method is attained by a method, which uses solid additional reductant floating on the copper surface with simultaneous bath stirring by the inert gas supplied by porous plugs.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a sketch illustrating schematically the principle of intensive, continuous fire refining of blister copper supplied from continuous Mitsubishi copper matte converting furnace.

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DETAILED DESCRIPTION OF INVENTION

30 This invention refers to a pirometallurgical method of oxygen removal from a liquid copper by the use of solid carboneous reductant, charged on the surface of copper in addition to the injection of reductant through tuyeres or lances and simultaneous agitation of copper bath with inert gas introduced via porous plugs. The method in which carboneous reductant and

hydrocarbons of oil or natural gas mixed with air or steam react with oxygen dissolved in copper results in high rate of reduction, shorten the time and increase of reductant efficiency.

Thus, the invention leading to a method of oxygen extraction from a liquid copper consists of following stages:

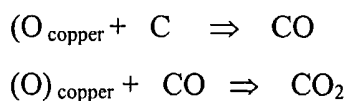
- a) Oxidation of copper bath to the level necessary for impurities removal;
- b) Addition of carboneous reductant onto copper surface, injection of the mix fuel reductat through tuyere(s) and agitation of bath by nitrogen via porous plugs;
- c) Continuation of oxygen extraction from a copper up to the desire oxygen content.

According to this invention, copper reduction (4), after oxidation and slagging of impurities, is carried out by injection of a liquid or gaseous reductant (oil, natutral gas) (3) with simultaneous addition of solid reductant (5) onto copper bath surface(4) and bath agitation with inert gas (1) through porous plugs (2)

Injection of a liquid or gaseous reductant with deficient amount of air (3) into the liquid copper (4) produces chemical reactions in the gaseous jet from tuyere and generated gas bubbles (9) rising up:

- Decomposition of hydrocarbons $C_nH_m \Rightarrow n C + m H_2$
- Partial combustion with air $2 C + O_2 \Rightarrow 2 CO$
 $2 H_2 + O_2 \Rightarrow H_2O$
- Reduction of copper $(O)_{copper} + C \Rightarrow CO$
 $(O)_{copper} + CO \Rightarrow CO_2$
 $(O)_{copper} + H_2 \Rightarrow H_2O$

Addition of charcoal or another solid carboneous reductant on the surface of copper bath initiates the reactions at the copper/carbon interface:





Injection of inert gas (1) through the porous plug (2) prevents the formation of the gradient of oxygen content in the copper slowing down the rate of reaction. Continuous stirring of the copper bath in whole volume by inert gas (1) ensures the mass transfer onto the reaction surface (copper/charcoal).

Simultaneous copper (4) reduction by injected reductant (oil, natural gas) and floating bed of charcoal or coke increases significantly the total process rate, decreasing the time of reduction and increasing furnace productivity.

Floating charcoal or coke bed (5) on the copper (4) surface allows for higher flexibility of burner operation. Even in the case of oxidising flame the charcoal (5) is protecting copper against the oxidation, permitting for more efficient use of fuel and better control of copper temperature. Moreover, the excess oxygen in the burner allows for post-combustion of reduction gases (7) leaving the bath producing clean gases.

The major problem of copper (4) reduction by injection of oil or natural gas (3) is the formation and emission of black fumes. Thermal decomposition of hydrocarbons produces hydrogen and elemental carbon (9). Carbon particles are partly reacting with oxygen from copper, but partly are rising up inside the bubbles being released from the melt. This part of carbon can be partly combusted over the melt if there is enough oxygen supplied by the burner. But, primary carbon monoxide is from reaction gases is combusting. Finally, significant part of carbon goes to chimney being emitted to the atmosphere. According to invention, floating bed of charcoal or coke on the copper surface acts as a filter for the carbon particles. The particles are caught by a filter, sintered and the carbon is used as a reductant together with charcoal. This leads to higher utilisation of carbon and higher reductant efficiency.

This invention has following advantages compared with traditional methods of copper reduction:

- a) Application of solid carbon addition combined with bath stirring by nitrogen introduced by porous plugs during injection of liquid or gaseous reductant significantly shorten reduction time from 40 to 60% in comparison to common reduction practice.
- b) Efficiency of reductant (carbon and hydrocarbons) increases from 30 to 50% of the average values of traditional operation.
- c) Emission of gases with black fumes (carbon black) is drastically decreased reducing negative process impact on the environment.
- d) Higher reductant efficiency and shorter reduction time results in the decrease of unitary reductant and fuel consumption as well as in the increase of furnace productivity.
- e) Cost of method application is low. Necessary modifications of refining furnace are minor.
- f)

EXAMPLE 1

Copper refining is carried out in vascular anode furnace capacity of 150 t of copper as it is schematically illustrated in Figure 1.. Four porous plugs (2) are mounted in the bottom part of the furnace. Through the porous plugs nitrogen (1) is injected into the molten copper (4). Nitrogen flowrate varies from 40 to 120 Nm³/h. Oxidation period is ended by skimming out of the slag. Oxygen content in the copper is in the level of 8000 ppm. Next, 1.5 to 4 kg of charcoal (5) per tonne of copper is charged through the mouth onto copper surface. Flow of oil through one tuyere is put on (about 4 - 8 kg/h per tonne of copper) together with air (4 - 8 Nm³/h per tonne of copper). Furnace is tilted and the tuyere immersed starting to blow into the copper. Oil flowrate is increased gradually up to the point that black fumes are not emitted. Setting of the burner is changed. Oil flowrate through the burner is shut down and air flow is kept at the level of 3 - 20 Nm³/h per tonne of copper. Introduced air through the burner ensures effective post-combustion of reduction gases leaving the bath. Charcoal on the surface prevents the copper against oxidation.

Produced off-gases leaving the furnace to a chimney are clean and acceptable for emission.

After 45 min of reductant injection through the tuyere oil flowrate is put gradually down and the furnace is tilted putting tuyere above the bath. Next, oil and air flow is shut down. Oxygen content in copper is 400 - 800 ppm and the furnace is prepared for anode casting.

5 EXAMPLE 2

Copper refining is carried out in stationary anode furnace of capacity 300 t of copper. Four porous plugs are installed in the bottom part of side wall against the wall with charging window. Nitrogen flowrate through porous plug is 0.3 – 1.0 Nm³/h per tonne of copper.

10 After finishing oxidation period and skimming out of refining slag the portion of 1.3 – 4.0 kg of charcoal per tonne of copper is charged through a window onto the copper surface. Next, the oil flow is put on through a lance (2 - 5 kg/h per tonne of copper) together with air (2 - 5 Nm³/h tonne of copper). Lance is immersed into the copper and reduction. Burner is supplied by natural gas. Burner parameters are set: 1 - 3 Nm³/h of natural gas and 7 - 20

15 Nm³/h of air per tonne of copper. It ensures effective post-combustion of reduction gases and emission of clean off-gas to the atmosphere. After 100 min the lance is removed and the oil and air flows shut down. Oxygen content has been decreased from 6000 - 8000 ppm to about 400 - 800 ppm. Next, anode casting is proceeded.

Claims:

1. An installation for continuous copper fire refining, said the system of reactors comprising the components:
 - (a) launder transferring liquid blister copper from continuous converting furnace or from retention furnace into the first oxidation reactor;
 - (b) copper oxidation reactor;
 - (c) optionally settler separating oxidized copper and slag;
 - (d) launder transferring oxidized copper from oxidation reactor into reduction reactor;
 - (e) copper reduction reactor;
 - (f) launder transferring reduced copper from reduction reactor to casting will or to retention-casting furnace;
2. A method as said forth in claim 1, said the flow of liquid copper is gravitational and continuous through oxidation reactor and reduction reactor.
3. A method as said forth in claim 1, wherein in step (b) said oxidation reactor is a vertical, cylindrical or rectangular furnace made of steel shell and refractories, equipped with tuyeres injecting air or the mix of fuel and air. The furnace has siphon or inclined tapping hole for continuous evacuation of oxidized copper and tapping hole for continuous tapping out of refining slag. The furnace is filled by packed bed of ceramic grains, or another chemically neutral grains, size of 2 – 100 mm in diameter.
4. A method as said forth in claim 1 and claim 3, said the oxidation furnace is equipped with bean and charging system for fluxes addition and system of reaction gases evacuation to the stack.
5. A method as said forth in claim 1 and claim 3, said oxidized copper and slag flows downwards creating after phase separation two layers on the furnace hearth. Slag and copper are evacuated through siphon and tapping hole. Optionally, the oxidized copper can be tapped out together and the separation can be carried out in a launder-settler.

6. A method as said forth in claim 1, wherein in step (e) said reduction furnace is a vertical, cylindrical or rectangular furnace made of steel shell and refractories, equipped with tuyeres injecting air or the mix of fuel and air. The furnace has siphon or inclined tapping hole for continuous evacuation of reduced copper. The furnace is filled by packed bed of charcoal grains, or coke grains of low sulphur content, size of 2 – 100 mm in diameter.

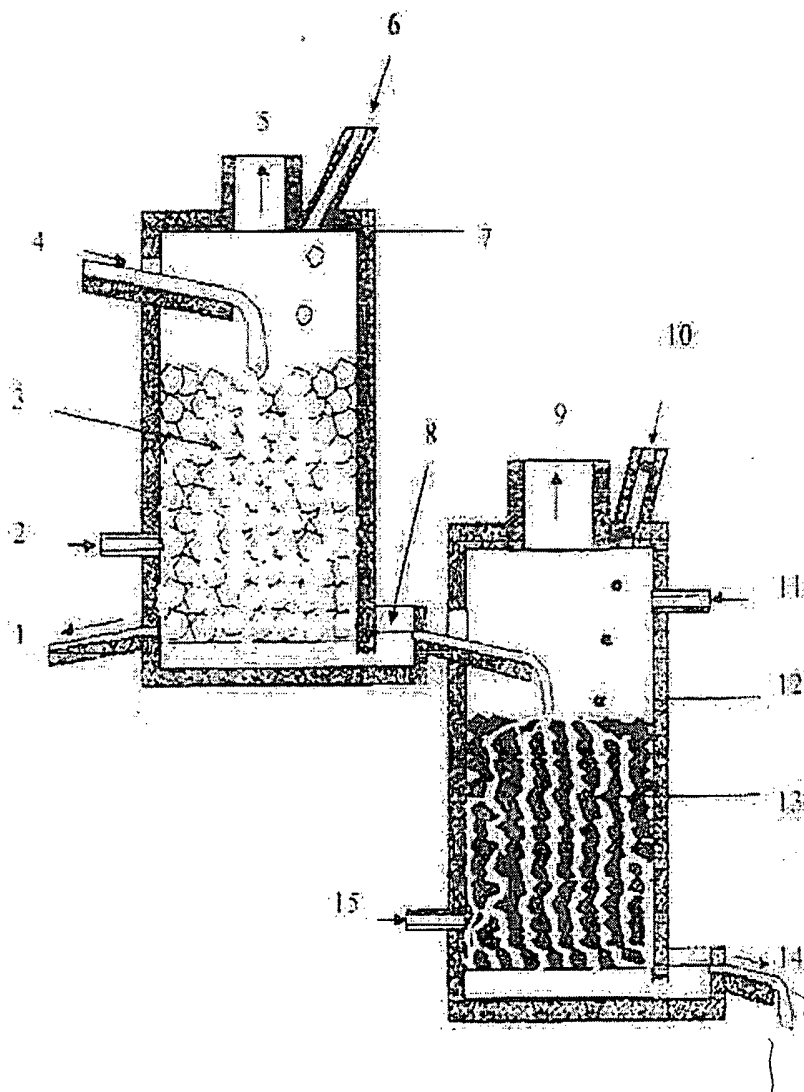


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/31945

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C22B 15/14

US CL : 266/162, 195

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 266/162, 195

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 practicable, search terms used)
WEST--search terms = (copper or cu) and (fire refin\$) and launder

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,315,775 A (ODLE et al.) 16 February 1982 (16.02.1982), see entire document.	1-3
Y		5
Y	US 3,868,248 A (NEU) 25 February 1975 (25.02.1975), see entire document.	6
A	US 5,449,395 A (GEORGE) 12 September 1995 (12.09.1995), see entire document	1-3, 6

☐ 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	"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
"E" earlier application or patent published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 December 2005 (12.12.2005)

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13 JAN 2006

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/31945

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. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ 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:
were not searched because they are improperly multiply dependent as covered by the second and third sentences of PCT Rule 6.4(a).
3. ☒ Claims Nos.: 4 and 5
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. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ 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.
- ☐ No protest accompanied the payment of additional search fees.