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(54) Water-soluble copper, copper alloys and non-ferrous metals intermediate cold and hot rolling composition

(57) The present invention relates to a water-soluble copper, copper alloys and non-ferrous metals intermediate cold and hot rolling composition comprising a base stock oil and, based on the total weight of the composition :

- from 1 to 80% by weight of a combination of
  - a monoester of a fatty acid with a polyol and
  - a tetraester of a fatty acid with pentaerythritol;

  the weight monoester : tetraester ratio of said combination ranging from 1:20 to 10:1; and

- from 0.02 to 2% by weight of an azole derivative.

The invention also relates to an oil-in-water emulsion, an intermediate cold rolling process, a hot rolling process and the use of the oil-in-water emulsion in an intermediate cold or hot rolling process.

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Brass Rolling
Rolling Force as a function of the Reduction Ratio per Pass
Rolling Speed : 120 m/min

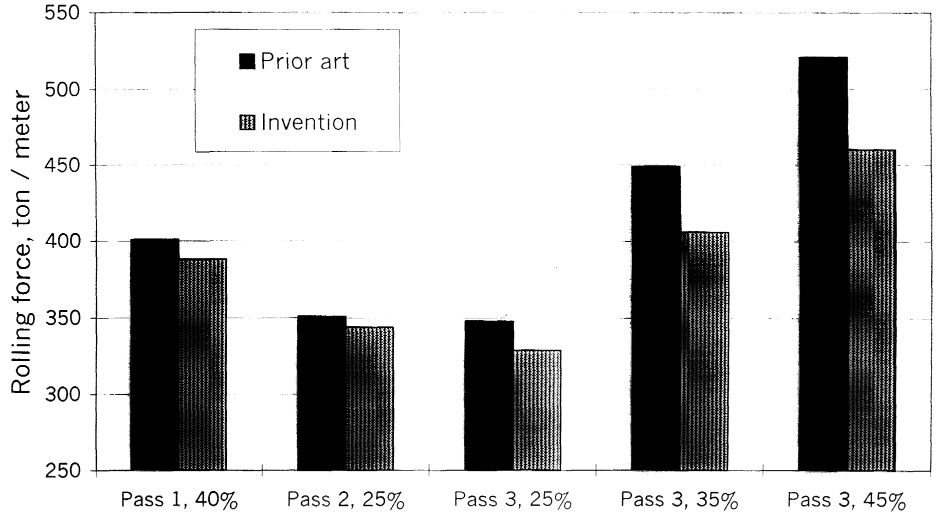

Fig. 2

Description

[0001] The present invention relates to a water-soluble copper, copper alloys and non-ferrous metals intermediate cold and hot rolling composition and to a process for intermediate cold or hot rolling copper, copper alloys and non-ferrous metals.

[0002] The copper, copper alloys and non-ferrous metals rolling industry expresses the need to maximize the efficiency of their rolled metal manufacturing process. In general terms, this means that there is a wish to operate at higher rolling speeds and to produce more marketable products per operating shift. Additionally, there is also a wish to minimize the number of passes through the mill taken to achieve a given level of reduction. Both these routes require that quality and surface finish be not compromised.

[0003] The invention thus provides an oil composition for rolling mills that enables to prepare emulsions which affords the following customer benefits:

- a high reduction ratio : one pass reduction is in most cases achievable;
- an excellent surface finish;
- an easy handling;
- a long charge life;
- a low oil consumption;
- a long emulsion life;
- a longer roll life; and
- a lower sensitivity to dissolved copper salts.

[0004] The invention is effective on any type of rolling, be it reversible or not, on breakdown, intermediate and finishing mills.

[0005] Especially, the invention exhibits high reduction and rolling capabilities while providing an excellent strip surface finish when rolling at high speed.

[0006] The prior art does not teach or even suggest the instant invention.

[0007] Thus, the invention provides a water-soluble copper, copper alloys and non-ferrous metals rolling oil composition comprising a base stock oil and, based on the total weight of the composition,

- from 1 to 80%, preferably from 1 to 30% by weight of a combination of

  - a monoester of a fatty acid with a polyol and
  - a tetraester of a fatty acid with pentaerythritol;
    the weight monoester : tetraester ratio of said combination ranging from 1:20 to 10:1, preferably from 1:10 to 5:1; and

- from 0.02 to 2%, preferably from 0.05 to 1% by weight of an azole derivative.

[0008] By "intermediate cold" is herein meant that the temperature is the ambiant temperature for the copper and copper alloy ingot.

[0009] By "hot rolling" is herein meant that the temperature is around 750°C for the copper and copper alloy ingot.

[0010] According to one embodiment, the oil composition further comprises, based on the total weight of the composition, from 0,1 to 20% of a mixture of ethoxylated alcohols (having from 5 to 15 carbons atoms and preferably from 12 to 15 carbon atoms). As an example of such a mixture, a mixture of ethoxylated alcohols sold by ICI under tradenames Synperonic® A7 and Hypermer® A60 can be used, the Synperonic® A7:Hypermer® A60 weight ratio preferably ranging from 1:10 to 10:1.

[0011] The invention further provides a process for preparing the oil composition.

[0012] The invention further provides an emulsion containing the oil composition and a process for preparing this emulsion.

[0013] In addition, the invention provides the use of the oil composition of the invention to prepare emulsions intended to be used in a copper, copper alloys and non-ferrous metals hot or cold intermediate rolling process.

[0014] The invention also provides a process for hot rolling copper, copper alloys and non-ferrous metals sheets, comprising applying an effective amount of the emulsion of the invention.

[0015] Finally, the invention provides the use of the emulsion in a hot rolling process or in an intermediate rolling process.

[0016] The invention is now disclosed in more details in the following specification.

[0017] Figure 1 shows the curves obtained when plotting the copper loss in weight (ppm) against the duration of the test in hours, when using an emulsion of the prior art and an emulsion of the invention.

[0018] Figure 2 is a graph showing the applied rolling force in ton/meter versus the number of passes, when using an emulsion of the prior art and an emulsion of the invention.

[0019] The oil compositions of the invention are neat oil concentrates generally intended to be diluted in water to give oil-in-water emulsions.

[0020] The base stock oil is any oil typically used in the field of intermediate cold or hot rolling. It can be paraffinic or naphthenic.

[0021] Paraffinic base oils are made from crude oils that have relatively high alkane contents (high paraffin and isoparaffin contents). Typical crudes are from the Middle East, North Sea, US mid-continent. The manufacturing process requires aromatics removal (usually by solvent extraction) and dewaxing. Paraffinic base oils are characterized by their good viscosity/temperature characteristics, i.e. high viscosity index, adequate low-temperature properties and good stability. They are often referred to as solvent neutrals, where solvent means that the base oil has been solvent-refined and neutral means that the oil is of neutral pH. An alternative designation is high viscosity index (HVI) base oil. They are available in full range of viscosities, from light spindle oils to viscous brightstock.

[0022] Naphthenic base oils have a naturally low pour point, are wax-free and have excellent solvent power. Solvent extraction and hydrotreatment can be used to reduce the polycyclic aromatic content.

[0023] A preferred base oil is an hydrotreated paraffinic neutral.

[0024] The base oil typically has a viscosity from 10 to 150 cSt at 40°C, preferably from 20 to 50 cSt at 40°C.

[0025] In the combination of the mono and tetra esters, the fatty acid of the monoester has from 16 to 20 carbon atoms and preferably is oleic acid. The polyol of the monoester is preferably glycerol.

[0026] The fatty acid of the tetraester has from 16 to 20 carbon atoms and preferably is oleic acid.

[0027] The azole derivative is generally selected from the group consisting of an aryltriazole, an arylimidazole and an arylthiazole.

[0028] Examples of an aryltriazole include benzotriazole, toluol triazole and toluyl triazole.

[0029] Examples of an arylimidazole include benzimidazole and 2-(5-aminopentyl) benzimidazole.

[0030] As arylthiazole , benzothiazole may be used.

[0031] Preferred azole is toluol triazole.

[0032] The oil composition may comprise classical additives, such as surfactants, coupling agents or cosurfactants, friction reducing agents or lubricity agents, corrosion inhibitors or anti-oxidants, extreme-pressure and anti-wear agents, bactericides and fungicides, anti-foaming agents, anti-rust agents.

[0033] However, an important feature of the invention is that the oil composition, and therefore also the emulsion, do not comprise nonyl-phenol surfactants, which are considered to raise environment problems.

[0034] Examples of anti-foaming agents are silicone based, especially polydimethylsiloxane.

[0035] Examples of corrosion inhibitors are hindered phenols and zinc dialkyldithiophosphates (ZDDP).

[0036] Examples of extreme-pressure and anti-wear agents are dilauryl phosphate, didodecyl phosphite, trialkylphosphate such as tri(2-ethylhexyl)phosphate, tricresylphosphate (TCP), zinc dialkyl(or diaryl)dithiophosphates (ZDDP), phospho-sulphurized fatty oils, zinc dialkyldithiocarbamate), mercaptobenzothiazole, sulphurized fatty oils, sulphurized terpenes, sulphurized oleic acid, alkyl and aryl polysulphides, sulphurized sperm oil, sulphurized mineral oil, sulphur chloride treated fatty oils, chlornaphta xanthate, cetyl chloride, chlorinated paraffinic oils, chlorinated paraffin wax sulphides, chlorinated paraffin wax, and zinc dialkyl(or diaryl)dithiophosphates (ZDDP), tricresylphosphate (TCP), trixylylphosphate (TXP), dilauryl phosphate, respectively.

[0037] Examples of corrosion inhibitors or anti-oxidants are radical scavengers such as phenolic antioxidants (sterically hindered), aminic antioxidants, organo-copper salts, hydroperoxides decomposers, butylated hydroxytoluene.

[0038] Examples of anti-rust agents are amine derivative of alkenyl succinic anhydride.

[0039] Further elements on base oils and additives can be found in "Chemistry And Technology Of Lubricants", R. M. Mortier and S.T. Orszulik, VCH Publishers, Inc, First published in 1992.

[0040] The following is an example of content of the water-soluble oil composition of the invention (the percentages are weight percentages based on the total weight of the composition) :

- 0.1-10% of trialkyl(C_{1-4})phenol;
- 0.5-4.0% of trialkyl(C_{3-10})phosphate ester;
- 1-4% of petroleum sulfonate;
- 0.1-0.5% of aminoalkyl (C_{2-3}) alkanediol (C_{2-3});
- 1-4% of trialkanol (C_{2-4})amine;
- 2-10% of a glycerol mono fatty acid (C_{16-20}) ester;
- 5-15% of pentaerythritol tetra fatty acid (C_{16-20}) ester;
- 0.5-1.0% of 5-carboxy 4-hexyl 2-cyclohexen 1-octanoic acid;
- 3-6 % of ethoxylated alcohols (C_{5-15}, comprising 2-10 CH_2O groups);

- 0.05-0.3% of triazole derivative;
- 0.05-0.4% of siloxan based polymer;
- the balance being a naphthenic lube base oil or a mixture of naphthenic base oils.

[0041] The water-soluble oil composition of the invention is prepared by blending the base oil and the other ingredients under stirring or with any mixing device, preferably whilst controlling the temperature so that is does not exceed 50°C, and more preferably 35°C.

[0042] An oil-in-water emulsion is prepared by diluting under stirring the oil composition of the invention in water.

[0043] An interesting feature of the invention is that it is possible to use hard water having up to 200 mg calcium carbonate per liter.

[0044] It is preferred to use deionized water which may previously have been warmed to around 35°C.

[0045] The emulsion generally comprises water and, based on the total volume of the emulsion, from 0.5 to 30%, preferably from 1 to 20%, by volume, of the oil composition.

[0046] The copper alloys to which the invention applies are any copper alloy, including brass and bronze alloys.

[0047] Examples of non-ferrous metals to which the invention applies are nickel and nickel alloys, zinc and zinc alloys.

[0048] The hot rolling process can be the classical process. It is generally carried out at a temperature of ingot 750°C.

[0049] The cold intermediate rolling process can be the classical process. It is generally carried out at ambient temperature.

[0050] The rolling process is preferably carried out on breakdown or finishing mills. The instant oil-in-water composition allows a significant reduction of the number of passes. With conventional prior art emulsions, the number of passes was typically 3-10. The emulsion of the invention allows lowering this number by 1 pass, which is a significant improvement.

[0051] When the rolling process is carried out in a breakdown mill, the emulsion preferably comprises, based on the total volume of the emulsion, from 2 to 3% by volume of the oil composition.

[0052] When the rolling process is carried out in a finishing mill, the emulsion preferably comprises, based on the total volume of the emulsion, from 4 to 7% by volume of the oil composition.

[0053] The following examples illustrate the invention without limiting it. All parts and ratios are given by weight, unless otherwise stated.

Example

[0054] A composition is prepared by mixing the ingredients of Table 1 in the order in which they appear in this table. The temperature is maintained at a maximum of 50°C to ensure a complete dissolution and homogeneisation of the ingredients without impairing the properties of the emulsion.

TABLE 1

Ingredients	Content (wt%)
Hydrotreated naphthenic base oil (20 cSt at 40°C)	33.50
Hydrotreated naphthenic base oil (110 cSt at 40°C)	39.50
Polydimethylsiloxane dispersed silica compound (defoamant)	0.10
Di-tertiobutyl paracresol (antioxidant)	0.20
Trioctylphosphate ester (extreme-pressure agent)	3.00
Petroleum sulfonate (surfactant)	2.80
Aminoethylpropanediol (buffer)	0.30
Triethanolamine (cosurfactant)	2.00
Glycerol monooleate ester (lubricity agent)	5.00
Pentaerythritol tetraoleate ester (lubricity agent)	8.40
5-carboxy 4-hexyl 2-cyclohexen 1-octanoic acid (corrosion inhibitor)	0.70
Ethoxylated alcohols * (surfactants)	4,50
Toluol triazole (corrosion inhibitor/copper passivator)	0.20

* : mixture of C_{12-15} alcohols :

- sold by ICI under the tradename Synperonic® A7 : 0,6%
- ethylene oxide addition polymer sold by ICI under the tradename Hypermer® A60 : 3,90%

[0055] The characteristics of the composition of Table 1 are set out in Table 2.

TABLE 2

Oil concentrate before dilution	Unit	Method	Typical characteristics
Colour (ASTM)		ISO 2049	L 2.0
Density at 15°C	G/ml	ASTM D 1298	0.9225
Pour point	°C	ISO 3016	-24
Viscosity at 40°C	CSt	ASTM D 445	48.6
Neutralization number	KOH mg/g	ASTM D 974	1.9
Saponification number	KOH mg/g	ASTM D 94	28.1
Total base number	KOH mg/g	ISO 3771	9.3

[0056] An emulsion is prepared by diluting under stirring the oil composition of Table 1 in deionized water prewarmed to 35°C. The characteristics of the obtained emulsion are given in Table 3.

TABLE 3

Emulsion	Method	Typical characteristics
Stability of the 6% (v/v) emulsion (at room temperature, for 20 hours)	Mobil [1)]	1.0% cream
pH value of fresh 6% (v/v) emulsion at 20°C	ASTM E 70-90	8.6

[1)] : The emulsion stability was determined according to the following procedure. 470 ml of distilled water at room temperature or test temperature were measured into a 800-ml beaker. A 50-ml stirrer having four paddles was attached to a stirring motor so that the paddles were positioned 25mm above the bottom of the beaker. A 50-ml dropping funnel was positioned such that the outlet was 15mm from the beaker wall. The stirrer was turned on and the rate adjusted to 1000 rpm. The sample was then heated up to a temperature of 35 ± 1°C. 30 ml of the test oil were added to the dropping funnel. The dropping rate was adjusted such that all the oil was transferred to the water within 120 ± 20 seconds. The stirring was then continued for an additional 60 seconds while the sample temperature was maintained at 35°±1°C. The resulting emulsion was poured into a 500-ml graduated cylinder and allow to stand at room temperature for 20 hours. After 20 hours, the upper layer (yellow cream + oil) was read in volume percent.

EXPERIMENTAL TESTING

[0057] A blank is first prepared by diluting a prior art oil composition which has the composition set out in Table 4 :

TABLE 4

Ingredients	Content (wt%)
Naphthenic base oil (100 cSt at 40°C)	39.0
Naphthenic base oil (22 cSt at 40°C)	36.0
Tap water	0.5
Petreoleum sulfonate	3.0
Amino ethyl alkanediol (C_3 to C_6)	0.3
Trioctyl phosphate ester	3.0
Trialkanol amine (C_2 to C_4)	1.0
5-carboxy 4-hexyl 2-cyclohexen 1-octanoic acid	0.7
Ethoxylated nonylphenol (5 ethylene oxide groups)	0.7
Ethoxylated nonylphenol (10 ethylene oxide groups)	2.4
Alkanol oleic acid ester (C_2 to C_{12})	13.4

[0058] Two emulsions are prepared by respectively diluting the oil compositions of the invention and of the prior art in dionized water.

[0059] Both emulsions are tested on copper to assess the surface finish improvement. The tests are carried out on copper strips in the following way.

[0060] All surface blemishes are removed from the test copper strips with silicon carbide paper. Each side is polished with silicon carbide grains picked with a pad of cotton moistened with iso-octane. The strips must be handled only with stainless steel forceps. After polishing, each strip is washed with iso-octane to remove the grains and immersed into fresh iso-octane. The strips are then removed from the wash solvent, dried with air and weighed to the nearest 0.1 mg. 500 ml of the test metal processing oil emulsion are prepared and 200 ± 1 g are weighed twice and each emulsion sample is introduced into a 250 mf flask.

[0061] The dry copper strips are then immersed into the flasks containing the emulsion samples and the flasked are corked. The flasked are placed into an oven at a temperature of 50°C for a given test period.

[0062] At the end of this period, the flasks are withdrawn from the oven. The strips are removed from the test emulsions, washed with acetone to remove water and with iso-octane to remove the oil. They are dried with air and then, weighed to the nearest 0.1 mg.

[0063] A further test cycle can be carried out by reimmersing the strips into the original test samples, corking the flasks and placing them into the ovent at the same temperature and for the same period as before.

[0064] The metal losses are then calculated for each strip as follows :

Loss in mg = M1 - M2
or
Loss in ppm = $(M1-M2)/M1 * 10^{-6}$
With :

M1 = strip weight before testing, in mg
M2 = strip weight after testing, in mg

[0065] Figure 1 shows the curves obtained when plotting the copper loss (or copper dissolution) in weight (ppm) against the duration of the test in hours.

[0066] As can be seen, with the emulsion of the invention the copper loss in much smaller than with the emulsion of the prior art, which means less chemical attack of the copper strip leading to a surface finish improvement.

[0067] The emulsions of the invention and of the prior art were then tested on brass to measure the rolling force improvement.

[0068] Figure 2 is a graph showing the applied rolling force in metric ton/meter versus the number of passes.

[0069] It can be seen that when the number of passes increases, the difference between the emulsion of the prior art and the emulsion of the invention increases, the rolling force being always smaller with the emulsion of the invention than with the emulsion of the prior art.

[0070] Since the lower the rolling force, the better the emulsion, it can be inferred that not only is the emulsion of the invention better than that of the prior art, but also the higher the number of passes, the better the emulsion of the invention as compared to the emulsion of the prior art.

Claims

1. Water-soluble copper, copper alloys and non-ferrous metals intermediate cold and hot rolling oil composition comprising a base stock oil and, based on the total weight of the composition :

   - from 1 to 80% by weight of a combination of

     - a monoester of a fatty acid with a polyol and
     - a tetraester of a fatty acid with pentaerythritol;
       the weight monoester : tetraester ratio of said combination ranging from 1:20 to 10:1; and

   - from 0.02 to 2% by weight of an azole derivative.

2. Water-soluble oil composition according to claim 1, further comprising, based on the total weight of the composition, from 0,1 to 20% of a mixture of ethoxylated alcohols having from 5 to 15 carbons atoms and preferably from 12

to 15 carbon atoms.

3. Water-soluble oil composition according to claim 1 or 2, comprising, based on the total weight of the composition, from 3 to 30% by weight of said combination.

4. Water-soluble oil composition according to any one of claims 1 to 3, comprising, based on the total weight of the composition, from 0.05 to 1% of said azole derivative.

5. Water-soluble oil composition according to any one of claims 1 to 4, wherein said weight monoester : tetraester ratio ranges from 1:10 to 5:1.

6. Water-soluble oil composition according to any one of claims 1 to 5, wherein the fatty acid of the monoester has from 16 to 20 carbon atoms and preferably is oleic acid.

7. Water-soluble oil composition according to any one of claims 1 to 6, wherein the polyol of the monoester is glycerol.

8. Water-soluble oil composition according to any one of claims 1 to 7, wherein the fatty acid of the tetraester has from 16 to 20 carbon atoms and preferably is oleic acid.

9. Water-soluble oil composition according to any one of claims 1 to 8, wherein the azole derivative is selected from the group consisting of an aryltriazole, an arylimidazole and an arylthiazole.

10. Water-soluble oil composition according to claim 9, wherein the aryltriazole is selected from the group consisting of benzotriazole, toluol triazole and toluyl triazole.

11. Water-soluble oil composition according to claim 9, wherein the arylimidazole is selected from the group consisting of benzimidazole and 2-(5-aminopentyl) benzimidazole.

12. Water-soluble oil composition according to claim 9, wherein the arylthiazole is benzothiazole.

13. Water-soluble oil composition according to claim 10, wherein the aryltriazole is toluol triazole.

14. Water-soluble oil composition according to anyone of claims 1 to 13, comprising (in weight percentages based on the total weight of the composition) :

- 0.1-10% of trialkyl (C_{1-4})phenol;
- 0.5-4.0% of trialkyl (C_{3-10}) phosphate ester;
- 1-4% of petroleum sulfonate;
- 0.1-0.5% of aminoalkyl (C_{2-3}) alkanediol (C_{2-3});
- 1-4% of trialkanol (C_{2-4})amine;
- 2-10% of a glycerol mono fatty acid (C_{16-20}) ester;
- 5-15% of pentaerythritol tetra fatty acid (C_{16-20}) ester;
- 0.5-1.0% of 5-carboxy 4-hexyl 2-cyclohexen 1-octanoic acid;
- 3-6 % of ethoxylated alcohols (C_{5-15}, comprising 2-10 CH_2O groups) ;
- 0.05-0.3% of triazole derivative;
- 0.05-0.4% of siloxan based polymer;
- the balance being a naphthenic lube base oil or a mixture of naphthenic base oils.

15. Water-soluble oil composition according to any one of claims 1 to 14, in which the base stock oil has a viscosity comprised between 10 and 150 cSt, preferably between 20 and 50 cSt at 40°C.

16. Oil-in-water emulsion comprising water and from 0.5 to 30%, preferably from 1 to 15% (v/v) of the water-soluble oil composition according to any one of claims 1 to 15.

17. Process for the preparation of a water-soluble oil composition according to any one of claims 1 to 15, comprising blending the base stock and the other ingredients under stirring or with any mixing device.

18. Process for the preparation of an oil-in-water emulsion according to claim 16, comprising diluting the oil composition in water under stirring.

19. Intermediate cold rolling process for rolling copper, copper alloys and non-ferrous metals sheets, comprising applying an effective amount of the emulsion according to claim 16.

20. Intermediate cold rolling process according to claim 19, wherein the rolling process is carried out in a breakdown mill and the emulsion comprises, based on the total volume of the emulsion, from 2 to 3% by volume of the water-soluble oil composition according to any one of claims 1 to 15.

21. Intermediate cold rolling process according to claim 19, wherein the rolling process is carried out in a finishing mill and the emulsion comprises, based on the total volume of the emulsion, from 4 to 7% by volume of the water-soluble oil composition according to any one of claims 1 to 15.

22. Hot rolling process for rolling copper, copper alloys and non-ferrous metals sheets, comprising applying an effective amount of the emulsion according to claim 16.

23. Hot rolling process according to claim 22, wherein the rolling process is carried out in a breakdown mill and the emulsion comprises, based on the total volume of the emulsion, from 2 to 3% by volume of the water-soluble oil composition according to any one of claims 1 to 15.

24. Hot rolling process according to claim 22, wherein the rolling process is carried out in a finishing mill and the emulsion comprises, based on the total volume of the emulsion, from 4 to 7% by volume of the water-soluble oil composition according to any one of claims 1 to 15.

25. Use of the water-soluble oil composition according to any one of claims 1 to 15 to prepare emulsions intended to be used in a copper, copper alloys and non-ferrous metals intermediate cold or hot rolling process.

26. Use of the water-in-oil emulsion of claim 16 in an intermediate cold or hot rolling process.

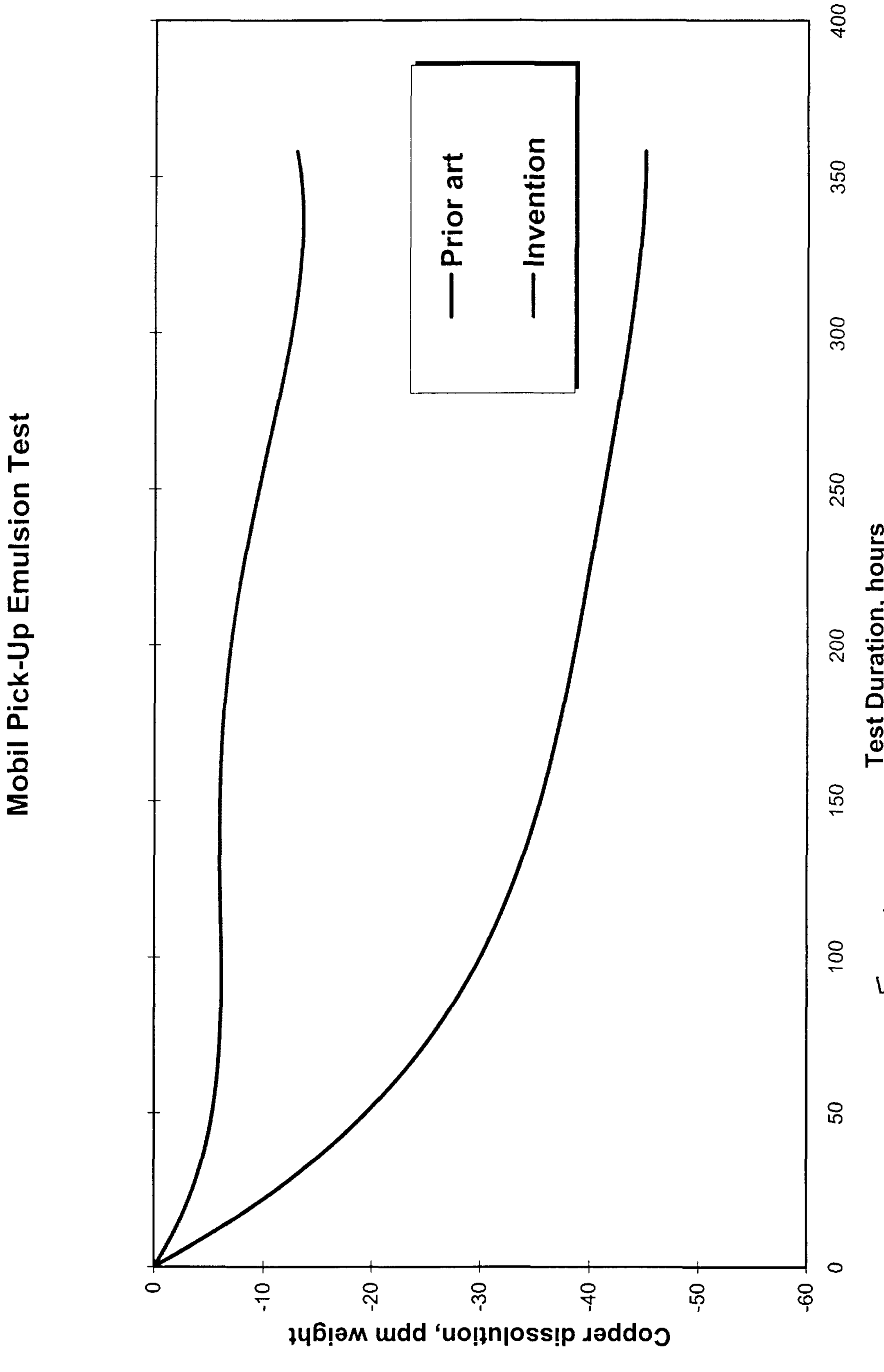
Mobil Pick-Up Emulsion Test
Copper dissolution, ppm weight
0
-10
-20
-30
-40
-50
-60
Test Duration, hours
0
50
100
150
200
250
300
350
400
Prior art
Invention

Fig. 1

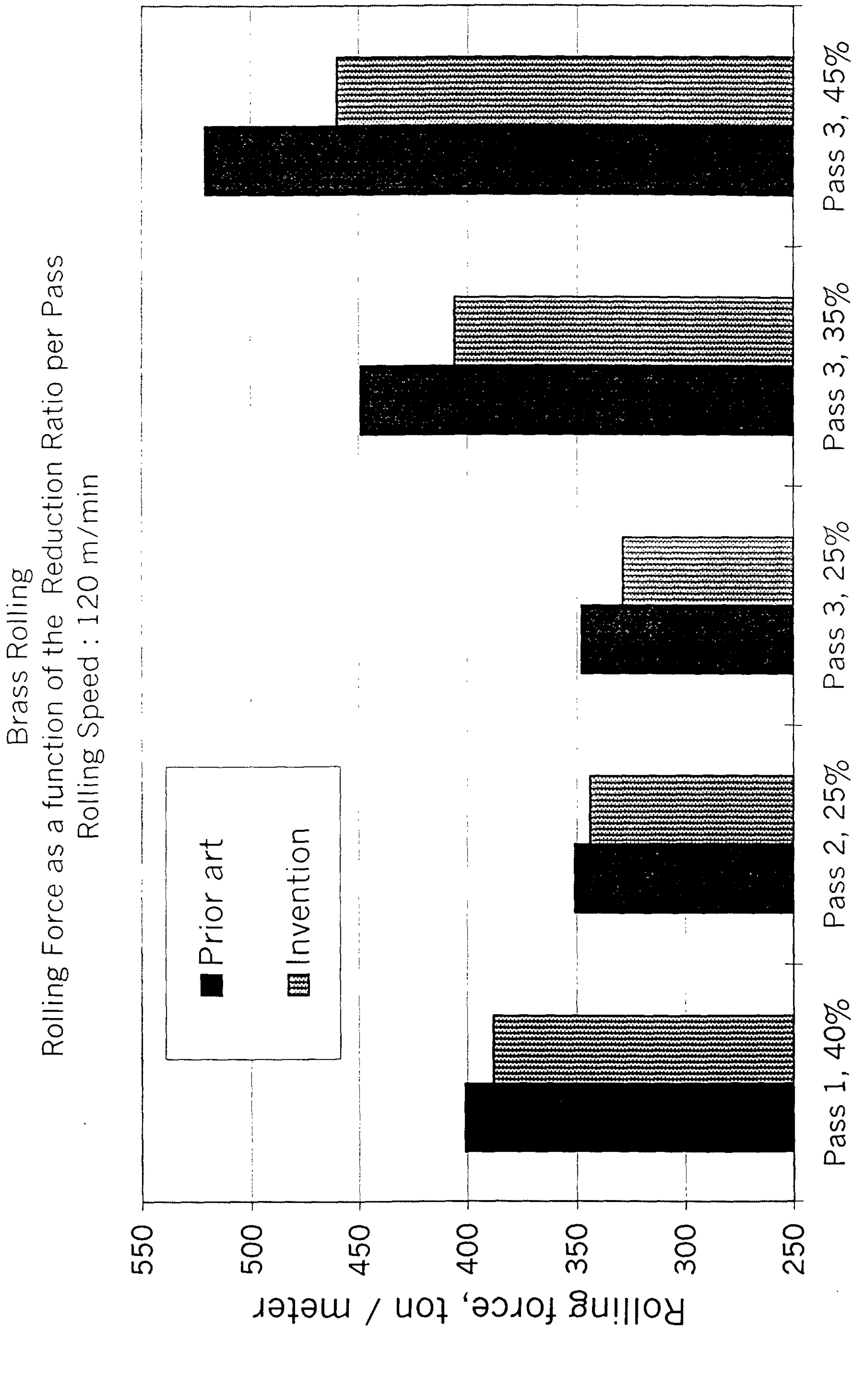
Brass Rolling
Rolling Force as a function of the Reduction Ratio per Pass
Rolling Speed : 120 m/min
Prior art
Invention
Rolling force, ton / meter
550
500
450
400
350
300
250
Pass 1, 40%
Pass 2, 25%
Pass 3, 25%
Pass 3, 35%
Pass 3, 45%

Fig-2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 40 0348

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 July 2000	Rotsaert, L

CATEGORY OF CITED DOCUMENTS

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E : earlier patent document, but published on, or after the filing date
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 40 0348

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