

(19)



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(11)

EP 1 123 970 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

16.08.2001 Bulletin 2001/33(21) Application number: **00400344.8**(22) Date of filing: **08.02.2000**(51) Int Cl.7: **C10M 173/00**, C10M 111/02,
C10M 169/04// (C10M173/00, 129:70,
159:04),

(C10M111/02, 101:02, 105:34),

(C10M169/04, 101:02, 129:70),

C10N40:24

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI(71) Applicant: **Mobil Oil Francaise****92400 Courbevoie (FR)**

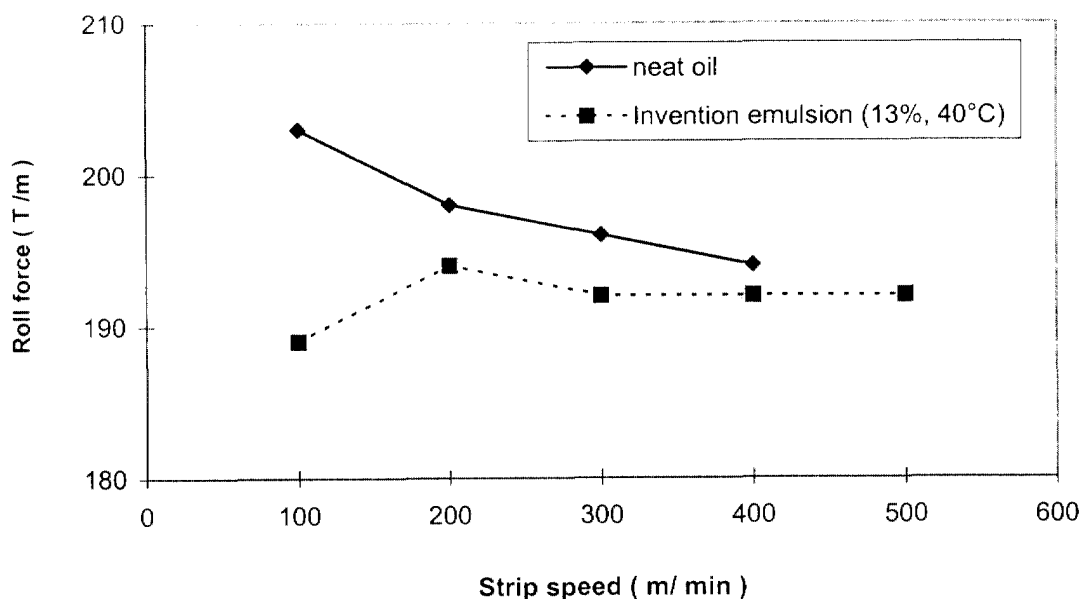
(72) Inventors:

• **Prince, Francis****76330 Notre Dame de Gravenchon (FR)**• **Chevolleau, Géraldine****45400 Fleury les Aubrais (FR)**(74) Representative: **Cabinet Hirsch****34, Rue de Bassano****75008 Paris (FR)**(54) **Water-soluble aluminium and aluminium alloys cold rolling oil composition**

(57) The present invention relates to a water-soluble aluminium and aluminium alloys cold rolling oil composition comprising a white mineral oil and, based on the total weight of the composition, from 10 to 95% of

an ester of a C₁₆₋₂₀ fatty acid and a C₂₋₆ alcohol.

The invention also relates to an emulsion containing the oil composition, to a process for cold rolling aluminium and aluminium alloys and to the use of the emulsion in an aluminium alloy cold rolling process.

**Fig. 1****EP 1 123 970 A1**

Description

[0001] The present invention relates to a water-soluble aluminium and aluminium alloys cold rolling oil composition and to a process for cold rolling aluminium and aluminium alloys.

[0002] The aluminium and aluminium alloys rolling industry expresses the need to maximize the efficiency of their cold 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] On the other hand, there is a need to increase mill safety by reducing the fire risks and the emissions of oil mists.

[0004] The invention thus provides an oil composition for cold rolling mills that enables to prepare emulsions which affords the following customer benefits:

- a high reduction ratio;
- a better rolling ability (i.e. a lower rolling force and a reduced power consumption) as compared to the rolling ability obtained with oil compositions of the prior art;
- a good surface finish quality;
- a high lubricity (plate-out properties, roll coating);
- a non-stained final product;
- a safer mill environment and better working conditions; and
- it can be used to prepare articles which are intended to be used in contact with food.

[0005] The invention is effective on any type of cold rolling, be it reversible or not, of the Sendzimir type (e.g. 1-2, 1-2-3, 1-2-3-4), or of Z-high type (e.g. 2-high, 4-high, 6-high), be it a reversible mill, a tandem mill, etc..

[0006] Especially, the invention exhibits high reduction and rolling capabilities while providing an excellent strip surface finish when rolling at high speed. The invention is also suited to Z-high rolling mill technology where high reduction ratio at low speed is obtained.

[0007] The prior art does not teach or even suggest the instant invention.

[0008] Thus, the invention provides a water-soluble aluminium and aluminium alloys cold rolling oil composition comprising a white mineral oil and, based on the total weight of the composition, from 10 to 95% of an ester of a C₁₆₋₂₀ fatty acid and a C₂₋₆ alcohol.

[0009] The invention further provides a process for preparing the oil composition.

[0010] The invention further provides an emulsion containing the oil composition and a process for preparing this emulsion.

[0011] In addition, the invention provides the use of the oil composition of the invention to prepare emulsions intended to be used in a aluminium or aluminium alloy cold rolling process.

[0012] The invention also provides a process for cold rolling aluminium and aluminium alloys sheets, comprising applying an effective amount of the emulsion of the invention.

[0013] Finally, the invention provides the use of the emulsion in an aluminium or aluminium alloy cold rolling process.

[0014] The invention is now disclosed in more details in the following specification and in reference to the drawings in which:

Figure 1 is a graph showing the roll force as a function of the strip speed at a constant reduction rate of 50%, when using the emulsion of the invention and a neat oil of the prior art;

Figure 2 is a graph showing the roll force as a function of the strip speed at a constant reduction rate of 60%, when using the emulsion of the invention and a neat oil of the prior art;

Figure 3 shows the surface of a strip after cold rolling with an emulsion of the invention;

Figure 4 shows the surface of a strip after cold rolling with a neat oil of the prior art;

Figure 5 is a graph showing the roll force as a function of the strip speed at a constant reduction rate, when using an emulsion of the invention at a concentration of 9% and with an emulsion of the invention at a concentration of 13%;

Figure 6 is a graph showing the roll force as a function of the strip speed at a constant reduction rate, when using an emulsion of the invention prepared at 25°C and an emulsion of the invention prepared at 40°C.

[0015] The water-soluble oil compositions of the invention are neat oil concentrates generally intended to be diluted in water to give oil-in-water emulsions.

[0016] By "white mineral oil", it is herein intended very highly refined oils which consist entirely of saturated compo-

nents, all aromatics having generally been removed by treatment with fuming sulphuric acid or by selective hydrogenation. Their name reflects the fact that they are virtually colourless and the most highly refined medicinal white oils are used in medical products and in the food industry.

[0017] The white mineral oils used in the invention are preferably those which can be safely used as a component of nonfood articles intended for use in contact with food. These oils are described in 21 CFR Ch. 1 §178.3620 (a) and (b) of the Food and Drug Administration, HHS.

[0018] Thus, the oil composition and emulsion according to the invention are adapted to be used as a component of nonfood articles intended for use in contact with food.

[0019] White oils are for example sold by the company SIP Limited of LONDON. A preferred white mineral oil is SPC 5L.

[0020] The white mineral oil typically has a viscosity from 4 to 30 cSt at 40°C, preferably from 4.5 to 6 cSt at 40°C. Viscosity can be adjusted by using a viscosity adjuster (such as kerosene), if needed.

[0021] In the water-soluble oil composition of the invention, the C₁₆₋₂₀ fatty acid used to form the ester preferably is stearic acid and the C₂₋₆ alcohol preferably is butanol, more preferably isobutanol.

[0022] The content of the ester, based on the total weight of the oil composition, preferably ranges from 50 to 85% by weight.

[0023] The water-soluble 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.

[0024] Examples of anti-foaming agents are silicone based, especially polydimethylsiloxane.

[0025] Examples of corrosion inhibitors are hindered phenols and zinc dialkyldithiophosphates (ZDDP).

[0026] 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.

[0027] 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.

[0028] Examples of anti-rust agents are amine derivative of alkenyl succinic anhydride.

[0029] Examples of friction reducing agents or lubricity agents are fatty alcohols having a carbon number in the range from 12 to 18, fatty esters having a carbon number in the range from 12 to 18, like glycerol monooléate.

[0030] 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.

[0031] The oil composition 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 it does not exceed 50°C, and more preferably, 40°C.

[0032] An oil-in-water emulsion is prepared by diluting under stirring the oil composition of the invention in water.

[0033] The water preferably is distilled water which has been prewarmed to a temperature of from 20° to 45°C, more preferably of from 20°C to 30°C.

[0034] The emulsion generally comprises water and, based on the total volume of the emulsion, from 0.5 to 30%, preferably from 10 to 15%, by volume, of the oil composition.

[0035] The aluminium alloys to which the invention applies are any aluminum alloys, including 1000, 2000, 3000, 5000, 6000, 7000 series.

[0036] The cold rolling process can be the classical process. The oil temperature is generally maintained at a temperature below 70°C, preferably below 40°C.

[0037] The process is preferably carried out on a breakdown rolling mill, on a tandem rolling mill or on a finishing rolling mill. The instant oil composition allows a significant reduction of the number of passes. With conventional prior art oils, the number of passes was typically 5 to 7. The oil composition of the invention allows lowering this number by 1 pass, which is a significant improvement.

[0038] The following examples illustrate the invention without limiting it. All parts and ratios are given by weight, unless otherwise stated.

Examples

[0039] 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 40°C to ensure a complete dissolution and homogenisation of the ingredients without impairing the properties of the emulsion.

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TABLE 1

Ingredients	Content (wt%)
Light white mineral oil (5.2 cSt at 40°C)	17.70
Isobutyl stearate (lubricity agent)	50.00
Coconut oil fatty acid (lubricity agent)	10.00
C ₁₈ alcohol (lubricity agent)	10.00
Aminoethylpropanol (corrosion inhibitor)	3.00
Hexylene glycol (coupling agent)	2.50
Ethoxylated dodecanol (surfactant)	3.00
Ethoxylated oleic acid (surfactant)	3.00
Ditertiarybutyl paracresol (anti-oxidant)	0.30
Benzisothiazolinone (biocide)	0.50

[0040] 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)		T60104 ISO 2049	L 0.5
Density at 15°C	g/ml	T60172 ASTM D 1298	872
Viscosity at 40°C	CSt	ASTM D 445	10.83
Saponification number	KOH mg/g	ASTM D 94	114

[0041] An emulsion is prepared by diluting under stirring the oil composition of Table 1 in distilled water at 40°C. The characteristics of the obtained emulsion are given in Table 3.

TABLE 3

Emulsion **	Method	Typical characteristics
Stability of the 13% (v/v) emulsion (at room temperature, for 20 hours)	Mobil ¹⁾	9% cream
pH value of fresh 13% (v/v) emulsion at 20°C	ASTM E 70-90	8.70

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

[0042] The used mill test was a non-reversing single stand 2high rolling mill with coiler and decoiler designed for 30 mm wide sheets, which can take up to 0.6 mm thick strips of about 1000 m length.

[0043] Roll diameter was 92 mm with surface roughness Ra of 0.4 micron. Strips of AA5182 approximately 30 mm wide by 0.55 mm thick, were rolled with each of the test products, with the maximum strip rolling speed being 600 m/min in this configuration.

a) Comparative tests

[0044] As prior art oil, a neat oil having a viscosity of 1.7 cSt at 40°C and comprising 90 wt % of high flash point desulfurized kerosene and 10 wt % of lauryl alcohol, was used.

[0045] The roll force as a function of the strip speed at a constant reduction rate was measured with the emulsion of Table 3 and with the neat oil of the prior art.

[0046] Figure 1 shows the results obtained with a reduction rate of 50%.

[0047] Figure 2 shows the results obtained with a reduction rate of 60%.

[0048] It appears from these figures that the emulsion of the invention brings a much better rolling performance than the prior art neat oil.

[0049] In addition, in both cases, the macroscopic surface finish of the rolled strip, as observed in a microscopic surface analysis, is brighter on the strip rolled with the emulsion of the invention, than on the strip rolled with the neat oil of the prior art.

[0050] Figures 3 and 4 show the results of the microscopic surface analysis of strips rolled with the emulsion of the invention (Fig 3) and with the neat oil of the prior art (Fig. 4). (Magnification : 200 times, reduction rate : 50%, speed : 400 m/min)

b) Emulsion concentration

[0051] The influence of the emulsion concentration on rolling performance was determined as follows.

[0052] The roll force as a function of the strip speed at a constant reduction rate (50%) was measured with the emulsion of Table 3 (13%) and with a second emulsion prepared in the same way, except that the concentration of the oil composition of Table 1 was only 9%.

[0053] The results are shown on Figure 5.

[0054] At low and high strip speeds, better results are obtained with the 13% emulsion.

c) Emulsion preparation temperature

[0055] The influence of the emulsion preparation temperature on rolling performance was determined as follows.

[0056] The roll force as a function of the strip speed at a constant reduction rate (50%) was measured with the emulsion of Table 3 (13%) and with an emulsion prepared in the same way as the emulsion of Table 3, except that the dilution was carried out at 25°C.

[0057] The results are shown on Figure 6.

[0058] It appears that both emulsions provide high similar rolling performances.

[0059] At low strip speed or when the best surface finish is desired, better results are obtained with the emulsion prepared at 40°C.

Claims

1. Water-soluble aluminium and aluminium alloys cold rolling oil composition comprising a white mineral oil and, based on the total weight of the composition, from 10 to 95% of an ester of a C₁₆₋₂₀ fatty acid and a C₂₋₆ alcohol.

2. Water-soluble oil composition according to claim 1, comprising, based on the total weight of the composition, from 50 to 85% of said ester.

3. Water-soluble oil composition according to claim 1 or 2, wherein the C₁₆₋₂₀ fatty acid is stearic acid.

4. Water-soluble oil composition according to any of claim 1 to 3, wherein the C₂₋₆ alcohol is a butanol.

5. Water-soluble oil composition according to claim 4, wherein the butanol is isobutanol.

6. Water-soluble oil composition according to any one of claims 1 to 5, in which the white mineral oil has a viscosity comprised between 4 and 30 cSt at 40°C, and preferably between 4.5 and 6 cSt at 40°C.

7. Oil-in-water emulsion comprising water and from 0.5 to 30%, preferably from 10 to 15% (v/v) of the water-soluble oil composition according to any one of claims 1 to 6.

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8. Oil-in-water emulsion according to claim 7, which is adapted to be used as a component of nonfood articles intended for use in contact with food.
- 5 9. Process for the preparation of a water-soluble oil composition according to any one of claims 1 to 7, comprising blending the white mineral oil and the other ingredients under stirring or with any mixing device.
10. Process according to claim 9, wherein the blending is carried out at a temperature which does not exceed 50°C, preferably 40°C.
- 10 11. Process for the preparation of an oil-in-water emulsion according to claim 8, comprising diluting the oil composition in water under stirring.
12. Process according to claim 11, wherein the water is distilled water prewarmed to a temperature of from 20° to 45°C, more preferably of from 20°C to 30°C.
- 15 13. Cold rolling process for rolling aluminium and aluminium alloys sheets, comprising applying an effective amount of the emulsion according to claim 7 or 8.
14. Cold rolling process according to claim 13, wherein the cold rolling process is carried out with an emulsion according to claim 7 or 8.
- 20 15. Use of the water-soluble oil composition according to any one of claims 1 to 6 to prepare emulsions intended to be used in a aluminium or aluminium alloy cold rolling process.
- 25 16. Use of the water-in-oil emulsion of claim 7 or 8 in a aluminium or aluminium alloy cold rolling process.

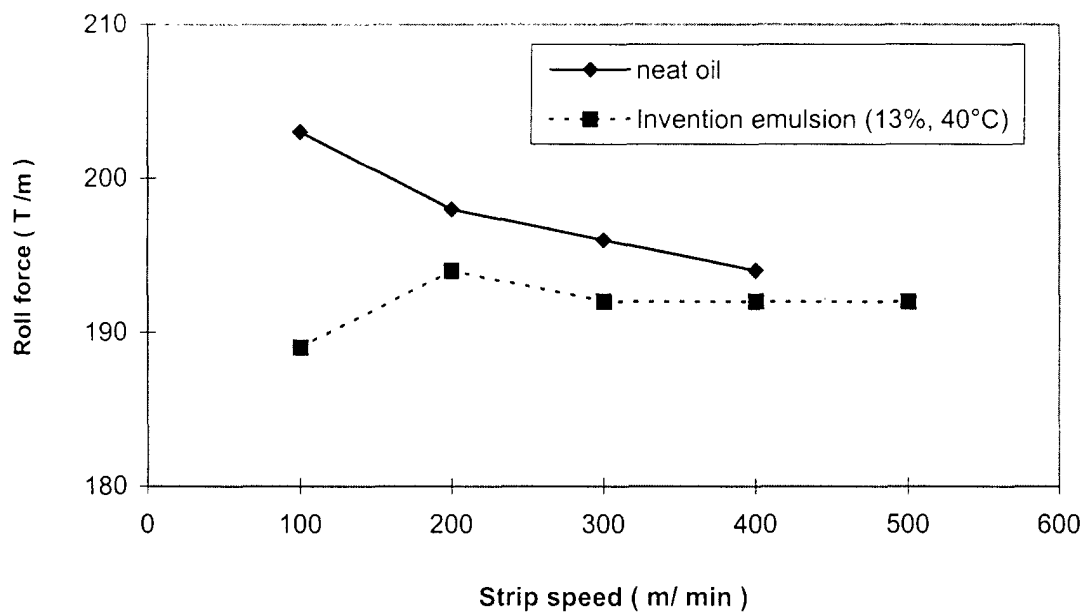


Fig. 1

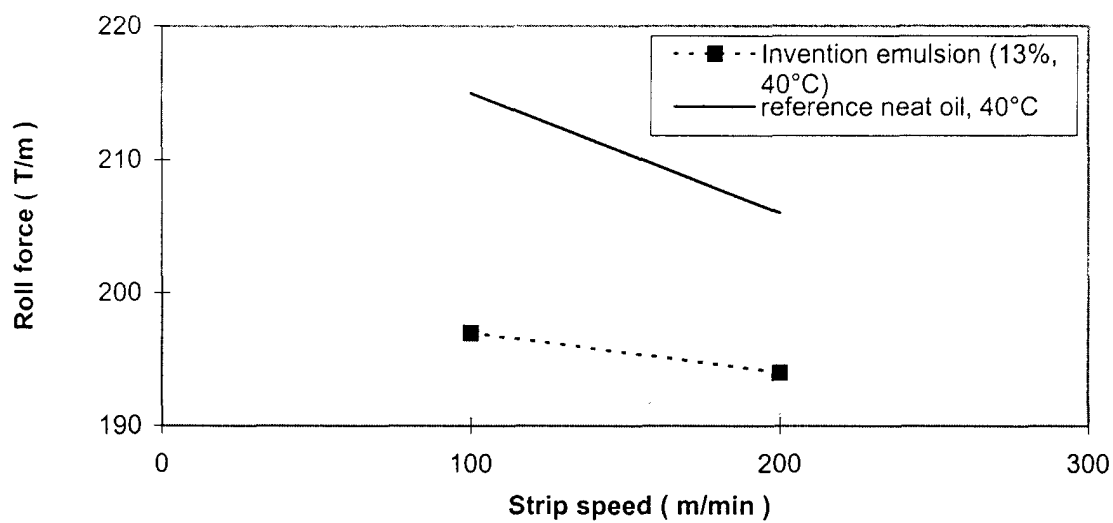


Fig. 2

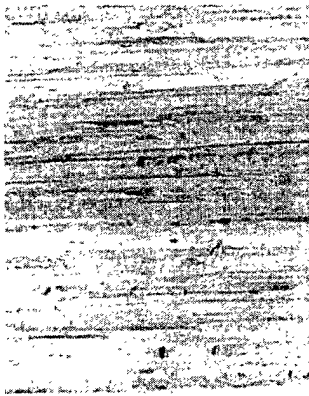


Fig. 3

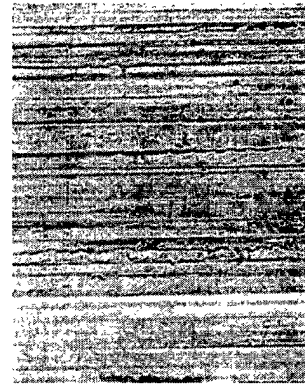
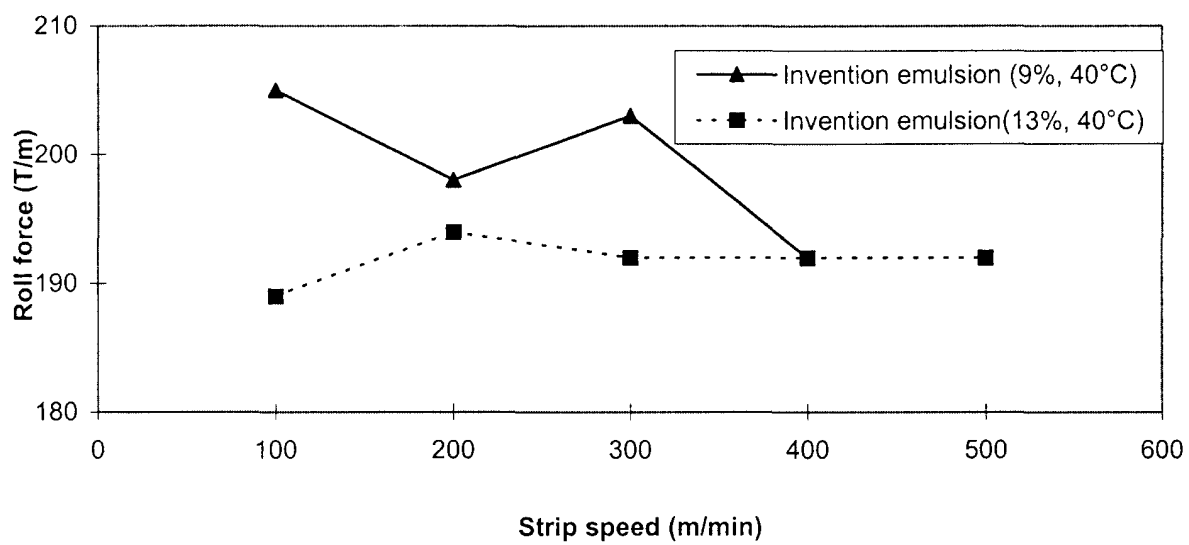
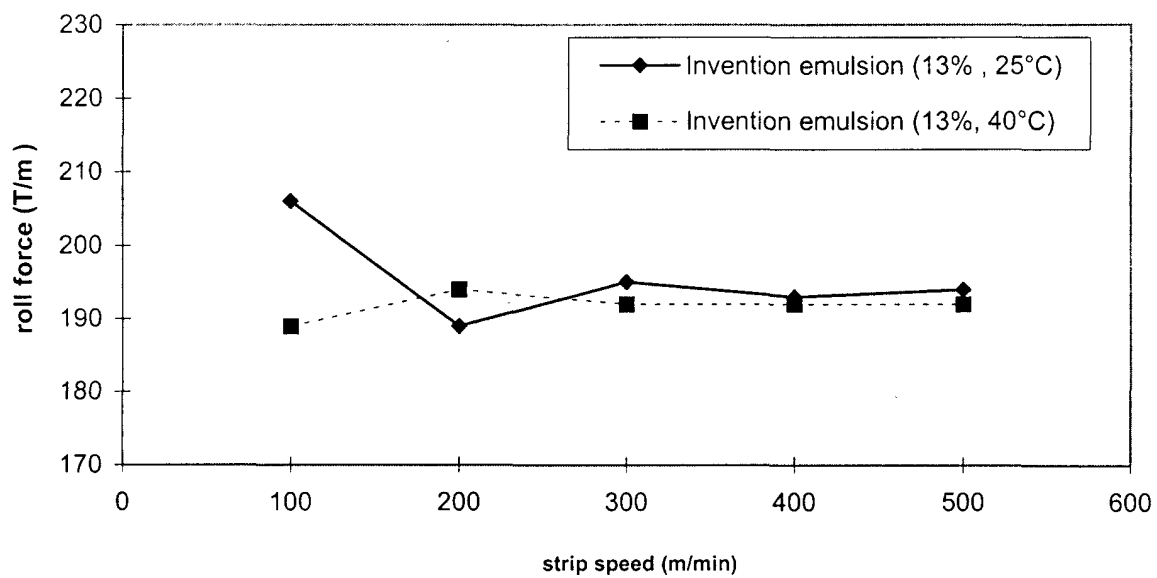


Fig. 4

Fig. 5Fig. 6



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EUROPEAN SEARCH REPORT

Application Number
EP 00 40 0344

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)
X	GB 1 369 515 A (EXXON RESEARCH ENGINEERING CO) 9 October 1974 (1974-10-09) * page 1, line 75 - page 2, line 23 * * page 3, line 15 - line 27 * * page 3, line 84 - line 92 *	1-16	C10M173/00 C10M111/02 C10M169/04 //(C10M173/00, 129:70, 159:04), (C10M111/02, 101:02, 105:34), (C10M169/04, 101:02, 129:70), C10N40:24
X	EP 0 315 873 A (IDEMITSU KOSAN CO) 17 May 1989 (1989-05-17) * page 2, line 7 - line 10 * * page 3, line 12 - line 39 * * page 3, line 51 - line 58 * * examples 1-4; table 2 *	1-16	
X	EP 0 332 433 A (GRACE W R & CO) 13 September 1989 (1989-09-13) * page 1, column 2, line 13 - line 52 *	1-16	
A	US 3 840 462 A (GERETZSCHLAGER M) 8 October 1974 (1974-10-08) * column 3; table 1 *	1-16	
A	GB 1 338 505 A (WITCO CHEMICAL CORP) 28 November 1973 (1973-11-28) * page 1, line 27 - line 33 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C10M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 June 2000	Examiner Rotsaert, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 40 0344

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23-06-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1369515	A	09-10-1974	AU 459402 A	27-03-1975
			AU 3853572 A	09-08-1973
			CH 588547 A	15-06-1977
			DE 2204599 A	09-08-1973
			FR 2168989 A	07-09-1973
EP 0315873	A	17-05-1989	JP 1123897 A	16-05-1989
			JP 2501217 B	29-05-1996
			DE 3867433 A	13-02-1992
			KR 9310573 B	28-10-1993
			US 4828731 A	09-05-1989
EP 0332433	A	13-09-1989	US 4882077 A	21-11-1989
			AU 3074589 A	14-09-1989
			BR 8901073 A	04-09-1990
			JP 1263194 A	19-10-1989
			NZ 228067 A	26-04-1991
US 3840462	A	08-10-1974	AT 323306 B	10-07-1975
GB 1338505	A	28-11-1973	BE 770766 A	01-12-1971
			DE 2137590 A	17-02-1972
			FR 2102095 A	07-04-1972
			JP 51033125 B	17-09-1976
			NL 7110652 A,B,	09-02-1972

EPO FORM P0450

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82