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COLD ROLLING AGENT

Shoji Shimada and Tohru Murase, Kitakyushu, Japan, assignors to Yawata Iron & Steel Co., Ltd., Tokyo, Japan

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14 Claims

ABSTRACT OF THE DISCLOSURE

A cold rolling lubricant for steel plates consisting of an aqueous solution of 0.1 to 10% by weight of at least one compound embraced by the formulas $A_n—P—(OH)_{3-n}$ and

$$A_n—\overset{\overset{O}{\|}}{P}—(OH)_{3-n}$$

wherein A is an organic radical and n is 1–2. The amine, ammonium, and alkali metal salts of the above compounds may also be used.

This invention relates to a cold rolling agent consisting of an almost transparent aqueous solution having dissolved therein a small amount of a water soluble organic phosphorus compound and also a cold rolling agent consisting of an emulsion, in which a rolling oil is emulsified in water, said rolling oil consisting of a base oil and an organic phosphorus compound added thereto.

In general, when a steel plate or a steel strip is subjected to cold rolling at a high speed, a cold rolling agent is supplied between rolling rolls and the steel plate or the steel strip in order to protect the surfaces of the steel plate or strip from being scratched at rolling and further in order to increase the rolling speed and to save the power necessary for the rolling.

For these purposes, there has hitherto been employed an oily cold rolling agent such as a mineral oil, an animal oil, the processed oil thereof, or an emulsion of the oil and water for cooling, and according to the kind of the rolling oil, rolling speed and rolling pressure, the cold rolling agent is in a fluid lubrication state, boundary lubrication state or a mixed state thereof between the rolling rolls and the steel plate or the stetel srip. As well known, the coefficient of friction of a steel plate or strip in the boundary lubrication at cold rolling is about 0.1, far larger than the coefficient of friction in the fluid lubrication, which is about 0.001. Accordingly, if a steel strip is cold rolled by the boundary lubrication mechanism, the rolling lubricating property of the boundary lubrication is lower than that of fluid lubrication and hence in order to prevent the reduction in rolling lubrication, an agent in use for a cold rolling of high reduction rate such as various higher aliphatic acids, higher amines, higher alcohols and the like is usually incorporated in the above-mentioned cold rolling oil.

In general, the cold rolled steel plate or strip is then annealed, but in the case of annealing it is in a state of a tight coil, unless the rolling oil, etc., attached to the surface of the steel strip or plate before annealing is removed therefrom by an electrolytic cleaning in an aqueous alkaline solution or by other powerful cleaning treatment, such black residues as carbon, iron powders and the like are attached to the surface of the steel strip or plate after annealing, which markedly destroys the appearance of the product steel plate or strip. Therefore, the application of the electrolytic cleaning or other cleaning treatment before annealing in a tight coil is inevitably necessary when using a conventional cold rolling oil. That is, if a rolled steel plate coil is annealed in a very

rigidly rolled up state, the evaporation of the rolling oil attached in a thin film to the surface of the steel plate is prevented even if the steel plate coil is heated to about 700° C. in an inert gas at annealing. Further by the catalytic actions of iron powders (worn out iron powders at rolling) present in the thin oil film and of the steel plate surface, the greater part of them are pyrolyzed to leave a large amount of black residues mainly composed of iron powders and carbon.

On the other hand, according to a so-called open coil annealing method in which a steel plate coil is annealed in a loosened state, there are no black residues on the surface of a steel strip even in the case of annealing a cold rolled steel strip having a thin oil film on the surface, and further the annealing can be finished in a shorter period of time than that in a tight coil type annealing system. However, in order to conduct such an open coil annealing process, a large quantity of installation cost is required, which makes the process uneconomical.

An object of the present invention is to provide a cold rolling agent consisting of an almost transparent aqueous solution or aqueous emulsion of an organic phosphorus compound showing a rolling property the same as or superior to that of a conventional cold rolling oil containing an agent utilized for a cold rolling operation of high reduction rate. The cold rolling composition of the present invention is characterized in that no black residues are left on the surface of the annealed steel plate coil even though the coil is, after rolling, annealed in a tight-coiled state. Therefore, it is not necessary to clean the surface of the coil by an added cleaning step such as an electrolytic cleaning process.

Another object of the present invention is to provide a cold rolling agent which is simultaneously excellent in rolling lubricating power and surface deterging power.

A further object of the present invention is to provide a cold-rolling agent consisting of an organic phosphorus compound dispersed in various kinds of base oils, which is superior in rolling lubricating power to any conventional oily cold rolling agent.

At first, a cold rolling agent consisting of an aqueous solution or an aqueous emulsion having dissolved therein a small amount of an organic phosphorus compound will be explained.

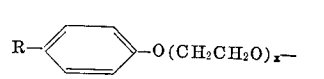
The cold rolling agent of the present invention comprises an aqueous solution or an aqueous emulsion having dissolved therein 0.1–10% by weight preferably 0.3–1% by weight of at least one member selected from the group consisting of the compounds represented by the following general formulas

$$A_n—\overset{\overset{O}{\|}}{P}(OH)_{3-n}$$

wherein A is an alkyl group having C_8 to C_{18} when n is 1, A is $RCOO—(CH_2.CH_2O)_x—$, RO^-, or

$$RO(CH_2CH_2O)_x—$$

wherein R is an alkyl group having 8 to 18 carbon atoms and x is 1 to 30 when n is 1–2; or A is



wherein R is an alkyl group having 8 to 10 carbon atoms and x is 0–30 when n is 1–2; and

$$A_n—P—(OH)_{3-n}$$

wherein A is RO^- where R is an alkyl group having 8 to 18 carbon atoms and n is 1–2; and/or at least one salt selected from a group consisting of ammonium, sodium, potassium and amine salts thereof.

The chemical structures of these compounds are shown more in detail as follows:

(I)

$$(RO)_n—P(=O)—(OH)_{3-n}$$

(alkyl acidic phosphoric acid esters)

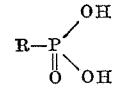
wherein R is an alkyl group having 8 to 18 carbon atoms, and n is 1–2; and/or the ammonium salts, sodium salts, potassium salts, or mono-, di- or tri-ethanolamine salts of the compound;

(II) $$(RO)_n—P—(OH)_{3-n}$$

(alkyl acidic phosphorus acid esters)

wherein R is an alkyl group having 8 to 18 carbon atoms and n is 1 or 2, and/or the salts of the compounds as in compound I;

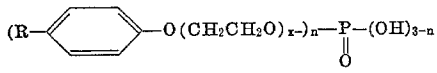
(III)



(alkyl phosphonic acids)

wherein R is an alkyl group having 8 to 18 carbon atoms and/or the salts thereof as in compound I;

(IV)



(alkylphenol polyethyleneoxide acidic phosphoric acid esters)

wherein R is an alkyl group having 8 to 9 carbon atoms, n is 1 or 2, and x is 0–30; and/or the salts thereof as in compound I;

(V)

$$\{RCOO(CH_2CH_2O)_{x-}\}_n—P(=O)—(OH)_{3-n}$$

(acid phosphoric acid esters of polyethylene oxide aliphatic acid esters)

wherein R is an alkyl group having 8 to 18 carbon atoms, n is 1 or 2 and x is 1–30, and/or the salts thereof as in compound I; and

(VI) $$\{RO(CH_2CH_2O)_{x-}\}_n—P(=O)—(OH)_{3-n}$$

(acid phosphoric acid esters of polyethylene oxide alkyl ethers)

wherein R is an alkyl group having 8 to 18 carbon atoms, n is 1 or 2, and x is 1–30, and/or the salts thereof as in compound I; and

(VII) Mixtures of at least two of compounds I to VI.

The properties of the above compounds as rolling agent are as follows.

The aqueous solution of the above mentioned compound, even of low concentration, has a rolling lubricatting property not inferior to that of a soluble type rolling oil emulsion of a mineral oil base that has hitherto been used in general. That is, by our experiments, it has been found that the rolling property of an aqueous solution containing about 0.3% of above-mentioned compounds I–VII is almost the same as that of a commercially available emulsion containing about 5 wt. percent of a mineral oil base soluble oil and can be effectively used as a rolling agent for a high-speed cold rolling having one-pass reduction rate of 10–20% and final rolling speed of 3000–4000 ft./min. Moreover, when the relation between the concentration of the compound and the rolling property was measured, it was found that the rolling lubricating property of compounds I to VIII was rapidly increased when the concentration is 0.2–0.3 wt. percent and thereafter, with the increase in concentration the lubricating power was gradually increased. These states are shown in Table 1 wherein the phosphoric acid monoester of polyoxyethylene nonyl-phenyl ether (HLB; 12) is compared with two kinds of commercially available rolling oils.

TABLE 1.—KIND OF COLD ROLLING AGENT AND ROLLING INDEX

Concentration of aqueous solution (wt. percent)	Cold rolling agent used/Rolling index: Aqueous solution of phosphoric acid monoester of polyoxyethylene nonylphenyl ether, percent	Commercial mineral oil base rolling oil emulsion (A), percent	Commercial mineral oil base rolling oil emulsion (B), percent
0.0 (water only)		9.0	
0.1	10.2	9.3	9.2
0.2	13.9		
0.3	14.3	10.3	10.6
0.5	14.5	11.5	11.7
1.0	14.4	12.3	12.0
2.0	14.6	13.4	13.9
3.0	14.8	14.1	14.5
5.0	14.6	14.2	14.6
10.0	15.1		
15.0	14.9		

NOTE.—Refer to the explanations of the methods of test and measurement of rolling index set forth in examples.

The surface conditions of the steel plate product rolled by using the rolling agent of this invention will be explained below. The rolling agent of this invention has completely different properties from conventional oil-base rolling oil in that the agent itself has surface active properties. Therefore, rolled materials are not stained at rolling, but rather iron powders (worn off powders of rolls and rolled materials) formed at rolling are positively cleaned and the surface of steel plate after rolling will be markedly cleaned. Further, in the case of repeatedly using a conventional oil emulsion as a rolling cooling liquid, the removal of iron powders admixed in the liquid is difficult and the stain of the liquid is increased as a result of the repeated use, and hence cleaning of the surface of the rolled steel plate is very difficult. On the other hand, since the cold rolling liquid of this invention is a transparent or slightly turbid white aqueous cleaning solution, the thus formed iron powders can be easily removed by means of centrifugal separator. Therefore, the cold rolling liquid can be easily maintained in clean state and hence the reappearance of stains to the rolled materials caused by the repeated use of the agent can be more easily prevented than with the use of conventional oil emulsions. Further, even if a steel plate rolled by using the cold rolling agent of the present invention is annealed by heating it in the tight coil state to about 700° C. in a conventional annealing gas atmosphere such as a DX gas or HNX gas without applying electrolytic cleaning or other cleaning, the surface of thus annealed steel plate is beautiful to an extent comparable with as the surface of a steel plate which is rolled by using a conventional oily cold rolling agent such as mineral oil and, which has been subjected to electrolytic cleaning, and annealed in the tight coil state as in the above case. If a more beautiful surface of the rolled steel plate is desired, the cold rolling may be conducted by using the cold rolling agent of the present invention in which the concentration of the addition compound is about 0.3% by weight. In particular, the above-mentioned compounds IV to VI are the most suitable additives since they contain a large amount of oxygen and hence they tend to form gaseous decomposition products during the annealing process, whereby the residues can be readily removed. In order to illustrate the advantage of the present invention, the surface properties of a steel plate cold rolled by the composition of the present invention is compared with the surface properties of a steel plate cold rolled by using a conventional oil cold rolling agent, and which has been treated by an electrolytic cleaning process. Further, the steel plate treated by the composition of the present invention has been compared with a steel plate which has simply been cold rolled by a conventional cold rolling agent. Likewise, the

surface stain of these steel plates after being annealed in a tight-coiled state are compared. The results are shown in Table 2.

TABLE 2.—SURFACE STAINS OF STEEL PLATE ROLLED BY SUPPLYING EACH COLD-ROLLING AGENT

Cold-rolling agent		Surface stain		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	Immediately after cold rolling	Immediately after electrolytic	Immediately after annealing
Tri-ethanolamine salt of phosphoric acid monoester of polyoxyethylene nonylpheny! ether.	0.3	94	(1)	97
	1.0	92	(1)	96
	5.0	92	(1)	96
Commercial mineral oil base rolling oil emulsion (A)	5 emulsion	68	98	96
Commercial mineral oil base rolling oil emulsion (B)	5 emulsion	72	97	97
Palm oil	15 emulsion	50	99	98

[1] Not carried out.

NOTE:
(1) Refer to the explanation of the method of measuring surface stain set forth in Examples.
(2) The surface stains of the steel plate rolled by using the emulsions of commercial oils A and B and then annealed without subjecting to an electrolytic cleaning were 70 to 80, and that of the case of using palm oil was 50 to 60.

As is clear from Table 2, the surface of the steel plate rolled by using the cold rolling agent of the present invention is, even though an electrolytic cleaning procedure is not applied, beautiful and the same as that of the steel plate which is cold rolled using a conventional cold rolling oil and then subjected to electrolytic cleaning. Therefore, if the cold rolling agent of the present invention is used, an electrolytic cleaning step or other washing step after cold rolling may be saved. This is one of main features of this invention.

As mentioned above, in the present invention there may be used an aqueous solution containing more than 0.2% by weight of above-described compounds I to VII but from the economical view point, it is suitable to use the aqueous solution containing about 0.2 to 10% by weight of said compound. The lower limit is defined to be 0.2% by weight since if the proportion of the compound is less than the value, the lubrication property for rolling is lowered and if the content is above 10% by weight, the lubricating property is not more improved, which is uneconomical. Thus, the most suitable range for the cold-rolling agent in practice is 0.3 to 1% by weight.

In addition, if the steel plate rolled by using the aqueous solution of the cold-rolling agent of the present invention tends to be rusted, there may be added to the cold-rolling agent of this invention a known rust preventing agent, such as, chromic acid, sodium bichromate, potassium bichromate, sodium sulfite, sodium pyrophosphate, sodium metaphosphate, sodium tripoly phosphate, sodium orthophosphate, and the like.

Thus, since the cold rolling agent of the present invention is an aqueous solution of the surface active agent, it exhibits a remarkable effect when it is used as a mill clean detergent.

In general, a mill clean detergent is used by blowing it between a steel plate and rolling rolls at the final pass of rolling for cleaning the surfaces of the steel plate and the rolling rolls. However, although a conventionally employed mill clean detergent has a deterging power, it has no rolling lubricating power and hence it must be used together with another rolling agent at the final pass of rolling. If in this case a conventional oily rolling agent is employed, the steel plate subjected to the final pass will naturally be attached with the oils, which cancels the worth of using the mill clean detergent.

On the other hand, since the cold rolling agent of the present invention is excellent in surface deterging power and rolling lubricating power, it can be effectively used as the mill clean detergent to be used by blowing at the end of cold rolling.

The present invention will now be explained by referring to the following examples in which the rolling index and the surface cleanness were measured as follows;

(A) ROLLING TEST

The rolling test was conducted by the following conditions and the rolling index was measured.

Rolling machine: Double rolling machine for testing.
Rolling roll: Surface bright finishing.
Interval between the upper and lower rolls: The interval was maintained constant through the whole rolling test.
Rolling material: Coiled soft steel plate having 0.26 mm. in thickness and 100 mm. in width.
Process for supplying rolling agent: An aqueous solution of the rolling agent was sprayed onto the roll and the steel strip at a pressure of 1 kg./sq. cm. directly before roll. When a commercially available cold rolling oil was sprayed onto a steel plate and then the steel plate was subjected to a conventional cold rolling, 0.2–0.5 g./sq. m. of the rolling oil was attached to the steel plate surface after cold rolling, but when the cold rolling agent of this invention was sprayed thereon, the amount of the agent attached to the plate was reduced to 1/10 to 1/20 of the amount of the above-mentioned conventional rolling oil attached thereto.
Measuring method of rolling property: A marking-off of 300 mm. in length was put on the steel material immediately before entered into the rolls, and after rolling the length of the marking-off was measured, from which the elongation percentage was determined.
Rolling speed: 13 m./min.

(B) MEASUREMENT FOR SURFACE CLEANNESS

An adhesive tape was attached to the surface of a steel plate sample and pressed sufficiently thereon. Then the tape was stripped and attached to a white paper. Thereafter, the thus attached tape was measured in respect to the reflection index by means of a colorimeter. In this case, the reflection index of a stain free tape attached to a white paper is defined to be 100 as a standard index. Thus, the more the measured reflection index is near 100, the less the surface stain of the steel plate is.

EXAMPLE 1

A steel plate was rolled using as the cold rolling agent an aqueous solution containing 0.3, 1.0 or 5.0% by weight of

$$C_{12}H_{25}-\underset{\underset{O}{\|}}{P}-(ONa)_2$$

and then annealed in the tight coil state. The results are shown in Table 3. Further, the surface cleanness of the steel plate cold rolled using this cold rolling agent is also shown in the table together with, for comparison, that of the steel plate cold rolled using an emulsion of a commercially available mineral oil base rolling oil A.

TABLE 3

Cold rolling agent		Rolling test result, Rolling index, (percent)	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)		Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of Example 1	0.3	13.9	93	(1)	97
	1.0	14.2	95	(1)	98
	5.0	14.3	92	(1)	95
Commercial mineral oil base rolling oil (A)	0.3 emulsion	10.3	85	99	97
	1.0 emulsion	12.3	74	98	97
	5.0 emulsion	14.3	68	98	96

[1] Not carried out.

EXAMPLE 2

A steel plate was rolled using as the cold rolling agent an aqueous solution containing 0.3, 1.0, or 5.0% by weight of

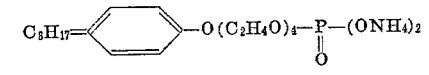
$$(C_8H_{17}O)_2—P—ONH(C_2H_4OH)_3$$

and then annealed in the tight coil state. The results are shown in Table 4.

Further, the surface cleanness of the steel plate cold rolled using the cold rolling agent is also shown in the table. In addition, the comparative experiment conducted by using an emulsion of a conventional mineral oil base rolling oil A is referred to in Table 3.

EXAMPLE 4

A steel plate was cold rolled by using as the cold rolling agent an aqueous solution containing 0.3, 1.0 or 5.0% by weight of



and then annealed in the tight coil state. The results are shown in Table 6.

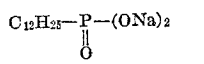
Further, the surface cleanness of the steel plate cold rolled by using the above cold rolling agent is shown therein. In addition, Table 3 illustrates a comparative case of using an emulsion of the commercially available mineral oil base rolling oil A.

TABLE 4

Cold rolling agent		Rolling test result, rolling index, percent	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)		Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of Example 2	0.3	12.8	95	Not carried out	98
	1.0	13.7	93	do	95
	5.0	14.2	90	do	96

EXAMPLE 3

A steel plate was cold rolled using the cold rolling agent an aqueous solution containing 0.3, 1.0, or 5.0% by weight of



and then annealed in the tight coil state. The results are shown in Table 5.

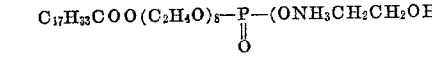
Further, the surface cleanness of the steel plate cold rolled by using the above-mentioned cold rolling agent is shown in the table. In addition, Table 3 refers to a comparative case of using an emulsion of a conventional mineral oil base rolling oil A.

TABLE 6

Cold rolling agent		Rolling test result, rolling index, percent	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)		Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of Example 4	0.3	14.1	95	Not carried out	97
	1.0	14.6	95	do	98
	5.0	14.3	93	do	96

EXAMPLE 5

A steel plate was cold rolled by using as the cold rolling agent an aqueous solution containing 0.3, 1.0, or 5.0% by weight of



and then annealed in the tight coil state, the results of which are shown in Table 7.

Further, the surface cleanness of the steel plate cold-rolled by using the above cold rolling agent is shown in

TABLE 5

Cold rolling agent		Rolling test result, rolling index, percent	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)		Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of Example 3	0.3	13.1	96	Not carried out	98
	1.0	14.5	95	do	96
	5.0	14.0	95	do	95

Table 7. In addition, Table 3 illustrates a comparative case of using an emulsion of a conventional mineral oil base rolling oil A.

TABLE 7

Cold rolling agent		Rolling test result,	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	Rolling index, percent	Immediately after cold rolling	Immediately after eectrolytic clleaning	Immediately after annealing
Rolling agent of Example 5	0.3	13.8	97	Not carried out	98
	1.0	14.7	95	do	99
	5.0	14.9	95	do	95

EXAMPLE 6

A steel plate was cold rolled by using as the cold rolling agent an aqueous solution containing 0.3, 1.0, and 5.0% by weight of

$$(C_8H_{17}O(C_2H_4O)_2-\underset{\underset{O}{\|}}{P}-ONH_2(CH_2CH_2OH)_2$$

and then annealed in the right coil state, the results of which are shown in Table 8.

Further, the surface cleanness of the steel plate cold rolled by using the above-prepared cold rolling agent is shown in the table. In addition, Table 3 sets forth a comparative case of using an emulsion of a conventional mineral oil base rolling oil A.

TABLE 8

Cold rolling agent		Rolling test result,	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	Rolling index, percent	Immediately after cold rolling	Immediate after electrolytic cleaning	Immediately after annealing
Rolling agent of Example 6	0.3	14.5	94	Not carried out	95
	1.0	14.7	93	do	96
	5.0	15.2	93	do	94

EXAMPLE 7

A steel plate was subjected to the rolling and annealing test as mentioned above by using 0.3, 1.0, or 5.0% by weight of an aqueous solution containing the rolling agent in Example 2 and the rolling agent in Example 6 in same proportion and results shown in the following table were obtained.

Further, the surface cleanness of the steel plate cold rolled by using the above-prepared cold rolling agent is shown in the same table. In addition, Table 3 sets forth a comparative case of using an emulsion of a conventional mineral oil base rolling oil A.

TABLE 9

Cold rolling agent		Rolling test	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	result, Rolling index, percent	Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Mixture of rolling agents in Examples 2 and 6 in same proportion	0.3	13.2	96	Not carried out	97
	1.0	14.5	95	do	98
	5.0	15.0	92	do	93

EXAMPLE 8

A steel plate was subjected to the cold rolling and annealing test as mentioned above by using as the cold rolling agent an aqueous solution containing 0.3, 1.0 or 5.0% by weight of

$$C_9H_{19}-C_6H_4-O(CH_2CH_2O)_{10}-\underset{\underset{O}{\|}}{P}-(OH)_2$$

and the results are shown in Table 10. Further, the surface cleanness of the steel plate cold-rolled by using the above-prepared cold rolling agent is shown in the same table. In addition, the results of using an emulsion of the commercially available mineral oil base rolling oil A are also shown.

EXAMPLE 9

A steel plate was subjected to the cold rolling and annealing test as above by using as the cold rolling agent an aqueous solution containing 0.3, 1.0, or 5.0% by weight of

$$C_{18}H_{35}O(CH_2CH_2O)_8-\underset{\underset{O}{\|}}{P}-(OH)_2$$

and the results are shown in Table 11. Further, the surface cleanness of the steel plate cold-rolled by using the above-prepared cold rolling agent is also shown in the same table. In addition, the results of using an emulsion of a commercially available mineral oil base rolling oil are referred in Table 10.

TABLE 10

Cold rolling agent		Rolling test	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	result, Rolling index, percent	Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Cold rolling agent of this Example	0.3	13.6	91	(1)	95
	1.0	14.0	93	(1)	96
	5.0	14.2	92	(1)	93
Commercially available mineral oil base rolling oil A	0.3 emulsion	10.3	85	99	97
	1.0 emulsion	12.3	74	98	97
	5.0 emulsion	14.2	68	98	96

[1] Not carried out.

TABLE 11

Cold rolling agent		Rolling test result,	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	Rolling index, percent	Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of this example	0.3	13.7	90	(1)	93
	1.0	13.9	89	(1)	97
	5.0	14.4	90	(1)	92

1 Not carried out.

EXAMPLE 10

A steel plate was subjected to the rolling and annealing test as above by using 0.3, 1.0, or 5.0% by weight of

$$C_{17}H_{33}COO(CH_2CH_2O)_{16}-\underset{\underset{O}{\|}}{P}-(OH)_2$$

and the results are shown in Table 12. Further, the surface cleanness of the steel plate cold-rolled by using the above-prepared cold rolling agent is also shown in the same table. In addition, the results of using an emulsion of a conventional mineral oil base rolling oil are referred in Table 10.

TABLE 12

Cold rolling agent		Rolling test result,	Surface cleanness		
Kind of rolling agent	Concentration of aqueous solution (wt. percent)	rolling index, percent	Immediately after cold rolling	Immediately after electrolytic cleaning	Immediately after annealing
Rolling agent of this example	0.3	14.0	94	(1)	97
	1.0	14.3	93	(1)	97
	5.0	14.7	94	(1)	96

1 Not carried out.

EXAMPLE 11

A steel strip was rolled by mean of a reversing rolling machine using a 5% emulsion of a conventional mineral oil base rolling oil for four passes and then was rolled at the fifth pass while spraying thereto an aqueous solution containing 0.3% by weight of the rolling agent as in Example 6, and it was observed the surface cleanness of the steel strip increased from 69 to 83. Further, when the above procedure was repeated by using an aqueous solution containing 0.3% by weight of a commercially available mill clean detergent, the cleanness increased from 71 to only 77.

Next, the second type of the cold rolling agent of the present invention, that is, the cold rolling agent, in which a rolling oil is dispersed and emulsified in water, said rolling oil consisting of a base oil and a small amount of an organic phosphorus compound added thereto, will be explained.

As a base oil for preparing the rolling oil mineral oils such as spindle oil, turbine oil, Diesel engine oil, motor oil, light oil, kereosene and the like, animal and vegetable oils such as palm oil, beef tallow, lard, rape oil, peanut oil, cotton oil, soy bean oil and the like may be used singly or in combination.

The organic phosphorus compounds to be added to the above mentioned base oil includes acidic phosphoric acid esters of polyoxyethylene alkylallyethers (carbon atoms in the alkyl group are 8 to 10 in number), acidic phosporic acid esters of polyoxyethylene alkylethers (carbon atoms in the alkyl group are 12 to 18 in number) and acidic phosphoric acid esters of polyoxyethylene fatty acid ester. The acidic phosphoric acid ester to be added to the base oil ranges from 0.2 to 10 wt. percent.

The rolling oil so prepared is emulsified in water in a ratio of 0.5 to 50%, preferably 3 to 25%.

The cold rolling agent of the emulsion type of the present invention has been proved to have a lubricating property much superior to any conventional rolling oil or emulsified lubricating agent in use for cold rolling, though with regard to the deterging property it is inferior to the cold rolling agent of the aqueous solution type of the present invention. However, even in the latter property it is still superior to the conventional ones, because the organic phosphorus compounds contained in the rolling agent of the present invention functions as a cleaner.

In preparing the rolling oil, however, it is necessary to cause the base oil and the organic phosphorus compound to dissolve with each other. In case of the dissolution being insufficient a dissolution promoting agent, such as polyoxyethylene alkylallylether, polyoxyethylene alkylether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester and the like, should be added to the base oil.

As occasion demands, conventional additives to be added to conventional rolling oils, covering monobasic fatty acids of a high degree such as lauric acid, palmitic acid, stearic acid, oleic acid, dibasic acids such as japanesque acid, alcohols of a high degree such as laurylalcohol, stearylalcohol, oleilalcohol or amines of high degree such as laurylamine, stearlyamine and the like, may be added, thereby the lubricating property of the rolling agent may be further improved.

EXAMPLE 12

A rolling oil was prepared by adding 3% polyoxyethylene sorbitan oleic acid ester (hereinafter it is called PEOESE) to a spindle oil #1, and another rolling oil which consists of 3% PEOESE and 2% phosphoric acid ester of polyoxyethylene oleilether (hereinafter it is called as PEOET) and the rest being the spindle oil.

These rolling oils were emulsified in water with the ratio of 10 wt. percent respectively.

The test result of the lubricating property of the thus emulsified cold rolling agent of the present invention, particularly in respect to frictional coefficient, pressure load resistance and rolling index, as compared with the emul-

sified rolling oil comprising no organic phosphorus compound, were shown in the following table.

TABLE 13

Number:	Composition of rolling oil: Component	Composition of rolling oil: Percent	Concentration of rolling oil in emulsion (percent)	Frictional coefficient [2]	Pressure load resistance (kg./cm.²)[2]	Rolling index (percent) [4]
1	Spindle oil 91	100	10	(1)	(1)	10.0
2	Spindle oil	97	10	0.175	3.0	10.3
	PEOESE	3				
3	Spindle oil	95				
	PEOESE	3	10	0.128	7.5	14.1
	PEOET	2				

[1] Measurement was not feasible due to the separation of oil component.
[2] Frictional coefficient was measured by the Soda's friction tester of the pendulum type.
[3] Pressure load resistance was measured by the Soda's tester of four ball type.
[4] For the rolling test, the surface bright finishing rolls were used, the distance between the rolls was maintained constant during rolling. Before rolling a marking-off of 300 mm. in length was put on a coiled soft steel plate of 0.26 mm. in thickness and 100 mm. in width, and after rolling the length of the marking off was measured to obtain the rolling index. At this time, the rolling agent was injected on the rolls and the steel plate.

EXAMPLE 13

A rolling oil was prepared by adding 5% acidic phosphoric acid ester of polyoxyethylene lauric acid ester (hereinafter it is called as PELES) to beef tallow.

The thus prepared rolling oil was emulsified in water in the amount of 10 wt. percent. The test results were shown in the following table.

TABLE 14

Number:	Composition of rolling oil: Component	Composition of rolling oil: Percent	Concentration of rolling oil in emulsion (percent)	Frictional coefficient	Pressure load resistance (kg./cm.²)	Rolling index (percent)
1	Beef tallow	100	10	(1)	(1)	15.3
2	Beef tallow	95	10	0.111	10.5	23.6
	PELES	5				

[1] Measurement was not feasible due to the separation of oil component.

As is seen from the above tables showing the test result of two examples, the cold rolling agent of the emulsion type comprising the organic phosphorus compounds of the present invention are all superior in the lubricating properties, as manifested by frictional coefficient, pressure load resistance and rolling index, to that comprising no organic phosphorus compound.

Making a summary of the results of the tests made on two types of the cold rolling agent of the present invention, that is, the cold rolling agent of the aqueous solution type containing no oily substance and that of emulsion type containing base oil, it is concluded that the former simultaneously possesses the lubricating and deterging properties, said lubricating property being equal or even superior to any conventional lubricating oil comprising lubricating additive, and the latter is particularly superior in lubricating property, though it is not equal in the deterging property to the former.

What we claim is:

1. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of at least one member selected from the group consisting of a compound represented by the following general formula

$$A_n-\underset{\underset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents an alkyl group having 8 to 18 carbon atoms and n is 1.

2. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of at least one member selected from the group consisting of a compound represented by the following general formula

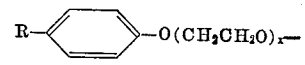
$$A_n-\underset{\underset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents a member selected from the group consisting of $R-COO(CH_2CH_2O)_x-$, $RO-$, and $RO(CH_2CH_2O)_x-$, where R is an alkyl group having 8 to 18 carbon atoms, and x is 1 to 30, and n is 1 to 2.

3. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of at least one member selected from the group consisting of a compound represented by the following general formula

$$A_n-\underset{\underset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents



where R is an alkyl group having 8 to 10 carbon atoms and x is 0 to 30, and n is 1 to 2.

4. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of at least one member selected from the group consisting of a compound represented by the following general formula

$$A_n-\underset{\underset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents RO— where R represents an alkyl group having 8 to 18 carbon atoms and n is 1 to 2.

5. A cold rolling agent in accordance with claim **1** which also contains at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts, and alkanolamine salts of the compounds defined in claim 1.

6. A cold rolling agent in accordance with claim **2** which also contains at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts, and alkanolamine salts of the compounds defined in claim **2**.

7. A cold rolling agent in accordance with claim **3** which also contains at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts, and alkanolamine salts of the compounds defined in claim **3**.

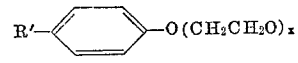
8. A cold rolling agent in accordance with claim **4** which also contains at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts, and alkanolamine salts of the compounds defined in claim **4**.

9. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of the sodium or potassium salt of at least one member

selected from the group consisting of a compound represented by the following general formula

$$A_n-\overset{\overset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents a member selected from the group consisting of an alkyl group having 8 to 18 carbon atoms, $R-COO(CH_2CH_2O)_x-$, $RO-$, $RO(CH_2CH_2O)$, where R is an alkyl group of 8 to 18 carbon atoms, and



where R' is an alkyl group having 8 to 10 carbon atoms, x is 0 to 30, and n is 1 to 2.

10. A cold rolling agent for steel plates which consists of an aqueous solution containing 0.1 to 10% by weight of at least one triethanolamine salt of the compounds represented by the following general formula

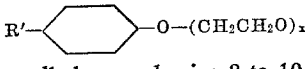
$$RO(CH_2-CH_2O)-\overset{\overset{O}{\|}}{P}-(OH)_2$$

where R is an alkyl group having C_8–C_{18}.

11. A method for manufacturing a cold rolled thin steel sheet comprising the steps of cold rolling the steel sheet by using a cold rolling agent consisting of an aqueous solution containing 0.1 to 10% by weight of at least one member selected from the group consisting of a compound represented by the following general formula:

$$A_n-\overset{\overset{O}{\|}}{P}-(OH)_{3-n}$$

wherein A represents a member selected from the group consisting of an alkyl group having 8 to 18 carbon atoms, $R-COO(CH_2CH_2O)_x-$, $RO-$, $RO(CH_2CH_2O)$, where R is an alkyl group of 8 to 18 carbon atoms and



where R' is an alkyl group having 8 to 10 carbon atoms, x is 0 to 30 and n is 1 to 2, rinsing the cold-rolled steel sheet to remove the lubricating coating formed on the surface of the steel sheet and then subjecting the cleaned steel sheet to an annealing treatment.

12. A method for manufacturing a cold rolled thin steel sheet according to claim **11** wherein the aqueous solution also contains at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts, and alkanolamine salts of the compounds defined in claim **11**.

13. A method according to claim **11** wherein the cold rolling agent is an aqueous solution of at least one salt selected from the group consisting of ammonium salts, sodium salts, potassium salts and alkanolamine salts of the compounds defined in claim **11**.

14. A cold rolling agent for steel plates which consists of an aqueous emulsion containing 0.1 to 10% by weight of at least one triethanolamine salt of the compounds represented by the following general formula:

$$RO(CH_2-CH_2O)-\overset{\overset{O}{\|}}{P}-(OH)_2$$

where R is a C_8–C_{18} alkyl group.

References Cited

UNITED STATES PATENTS

2,340,331	2/1944	Knutson et al.	252—49.8
2,420,602	5/1947	Kingerley	252—49.8 XR
2,957,931	10/1960	Hamilton et al.	252—49.8 XR
2,536,685	1/1951	Harman et al.	252—49.8 XR
2,917,459	12/1959	Reamer	252—49.3
2,991,244	7/1961	Pattenden et al.	252—32.5 XR
3,010,903	11/1961	Clarke et al.	252—49.8 XR
3,203,895	8/1965	Latos et al.	252—49.5 XR
3,233,442	**2/1966**	Zvanut	252—32.5 XR
3,277,001	10/1966	Fischer et al.	252—49.3 XR
3,310,489	3/1967	Davis	252—49.3 XR
3,320,164	5/1967	Brunel	252—32.5 XR
3,346,670	10/1967	Papalos	252—49.8 XR

DANIEL E. WYMAN, Primary Examiner

I. VAUGHN, Assistant Examiner

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