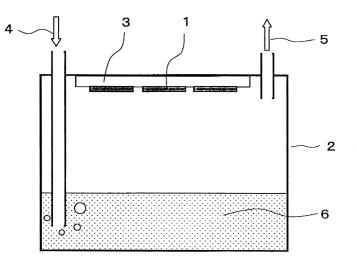
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# (54) CORROSION-RESISTANT STEEL MATERIAL FOR CRUDE OIL TANKER

(57) This invention provides a corrosion-resistant steel product for tanker that is excellent in the corrosion resistance in a corrosion environment of oil tanks of tankers and also excellent in the corrosion resistance after coating in a corrosion environment of ballast tanks. Specifically, this invention provides a corrosion-resistant steel product for crude oil tanker containing, by mass%, C: 0.03 to 0.16%, Si: 0.05 to 1.50%, Mn: 0.1 to 2.0%, P:

0.025% or lower S: 0.01% or lower, AI: 0.005 to 0.10%, N: 0.008 % or lower, Cr: more than 0.1% and 0.5% or lower, and Cu: 0.03 to 0.5% and, as an alternative addition element, one or two or more elements selected from W: 0.01 to 0.5%, Mo: 0.01 to 0.50, Sn: 0.001 to 0.2%, Sb: 0.001 to 0.5%, Ni: 0.005 to 0.3%, and Co: 0.005 to 0.3%, and further containing Cu, W, Mo, Sn, Sb, Cr, Ni, Co, S, and P in such a manner as to satisfy a specific relationship.

FIG. 1



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## Description

**Technical Field** 

<sup>5</sup> **[0001]** The present invention relates to corrosion-resistant steel products for crude oil tanker for use in different corrosion environment portions, such as oil tanks or ballast tanks of crude oil tankers. Specifically, the present invention relates to corrosion-resistant steel products for crude oil tanker capable of suppressing local corrosion occurring in the bottom plate of oil tanks of crude oil tankers and general corrosion occurring in the top board or the side plate thereof and further corrosion occurring in the coated surface of the ballast tanks on the back side of the bottom plate of oil tanks.

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Background Art

**[0002]** It is known that the inner side of the upper portion of oil tanks of crude oil tankers (back side of upper deck) causes general corrosion due to corrosive gas, such as  $H_2S$ , volatilizing from  $O_2$ ,  $CO_2$ , and  $SO_2$  contained in inert gas (exhaust gas of boilers, engines, or the like having a typical composition of  $O_2$ : 5 vol%,  $CO_2$ : 13 vol%,  $SO_2$ : 0.01 vol%, and  $N_2$ : balance) contained in the tanks for explosion protection or crude oil.

**[0003]** The  $H_2S$  is oxidized by catalyst action of iron rust generated by corrosion to become a solid S (elemental sulfur) and is present in the form of a layer in the iron rust. These corroded products are easily separated to be deposited on the bottom of crude oil tanks. Therefore, in tanker dock inspection performed every 2.5 years, maintenance and repair of the upper portions of tanks and removal of deposits are performed with considerable expense.

- **[0004]** In contrast, hitherto, it has been considered that steel products for use in the bottom plate of crude oil tanks of tankers are not corroded due to corrosion inhibition function of crude oil itself or corrosion inhibition function of a protective film derived from crude oil generated in the inner side of crude oil tanks. However, recently, it has been becoming clear that also steel products for use in the bottom plate of tanks causes bowl-shaped local corrosion.
- <sup>25</sup> **[0005]** Examples of the causes for the bowl-shaped local corrosion include:
  - (1) Presence of brine in which salts typified by sodium chloride are dissolved with a high concentration,
  - (2) Separation of a crude oil protection film due to excessive washing,
  - (3) Increase in the concentration of sulfides contained in crude oil,
  - (4) Increase in the concentration of  $O_2$ ,  $CO_2$ , and  $SO_2$  contained in inert gas for explosion protection, and (5) Participation of microorganisms.

However, the causes are just estimated, and clear causes have not been found.

- [0006] The most effective method for suppressing the above-described corrosion is subjecting the surface of steel products to heavy coating for protecting the steel products from the corrosion environment. However, it has been pointed that the heavy coating of crude oil tanks need considerable expense for coating or inspection because the coating area becomes large or in the corrosion environment of crude oil tanks, when heavy coating is carried out, corrosion of a damaged coating film portion is promoted on the contrary.
- [0007] Then, steel exhibiting corrosion resistance also under the corrosion environment, such as in crude oil tanks, has been proposed. For example, Patent Literature 1 discloses corrosion resistant steel for cargo oil tanks excellent in general corrosion resistance or local corrosion resistance in which, to a steel containing C: 0.01 to 0.3 mass%, Si, Mn, P, and S are added in a proper amount, Ni: 0.05 to 3 mass% is further added, and Mo, Cu, Cr, W, Ca, Ti, Nb, V, and B are selectively added. Patent Literature 1 discloses that, in a dry-wet repeated environment containing H<sub>2</sub>S, when the Cr content exceeds 0.05 mass%, the general corrosion resistance and the pitting corrosion resistance remarkably decrease, and thus the Cr content is lower than 0.05 mass%.
- decrease, and thus the Cr content is lower than 0.05 mass%.
   [0008] Patent Literature 2 discloses a corrosion resistant steel for crude oil tanks that has excellent general corrosion resistance and local corrosion resistance and also can suppress generation of corroded products containing a solid S in which, to a steel containing C: 0.001 to 0.2 mass%, Si, Mn, P, and S are added in a proper amount and Cu: 0.01 to 1.5 mass%, A1: 0.001 to 0.3 mass%, and N: 0.001 to 0.01 mass% are added, and further at least one of Mo: 0.01 to
- 50 0.2 mass% or W: 0.01 to 0.5 mass% is added.
  [0009] In contrast, the ballast tanks of crude oil tankers is under a very severe corrosion environment because the ballast tanks have a function of allowing safety navigation of vessels when there is no cargo and also, in the ballast tanks, seawater is poured therein. Therefore, for protecting corrosion of steel products for use in the ballast tanks, the formation of a protecting coating using an epoxy type paint and electrolytic protection are usually used in combination.
- <sup>55</sup> **[0010]** However, even when the corrosion protection measures are taken, the corrosion environment of the ballast tanks is still in a severe state. More specifically, when seawater is poured in the ballast tanks, a portion that is completely immersed in the seawater can be prevented from the progress of corrosion due to the function of electrolytic protection. However, when seawater is not poured in the ballast tanks, the electrolytic protection does not work at all. Thus, the

ballast tanks are subjected to severe corrosion due to the action of residual attached saline matter.

**[0011]** Some steel products for use in portions in severe corrosion environments, such as in the ballast tanks, have been proposed. For example, Patent Literature 3 discloses a corrosion-resistant low alloy steel for ballast tanks in which, to a steel containing C: 0.20 mass% or lower, Cu: 0.05 to 0.50 mass% and W: 0.01 to lower than 0.05 mass% are added

- <sup>5</sup> as a corrosion-resistance improvement element, and further one or two or more of Ni, Ti, Zr, V, Nb, Ge, Sn, Pb, As, Sb, Bi, Te, and Be is/are added. Patent Literature 4 discloses a corrosion-resistant low alloy steel for ballast tanks in which, to a steel products containing C: 0.20 mass% or lower, Cu: 0.05 to 0.50 mass% and W: 0.05 to 0.5 mass% are added as a corrosion-resistance improvement element, and further one or two or more of Ge, Sn, Pb, As, Sb, Bi, Te, and Be is/are added in a proportion of 0.01 to 0.2 mass%. Patent Literature 5 discloses a corrosion-resistant low alloy steel for
- <sup>10</sup> ballast tanks in which Cu: 0.05 to 0.15 mass% and W: 0.05 to 0.5 mass% are added to a steel containing C: 0.15 mass% or lower.

**[0012]** Patent Literature 6 discloses a ballast tank in which a protecting paint, such as a tar epoxy paint, a pure epoxy paint, a solventless epoxy paint, or a urethane paint, is applied to a low alloy corrosion-resistant steel product in which P: 0.03 to 0.10 mass%, Cu: 0.1 to 1.0 mass%, and Ni: 0.1 to 1.0 mass% are added as a corrosion-resistance improvement

- <sup>15</sup> element to a steel containing C: 0.15 mass% or lower for resin coating the low alloy corrosion-resistant steel product. This technique aims at extending the life of a protecting coating due to an improvement of corrosion resistance of the steel product itself to achieve maintenance-free over 20 to 30 years, during which vessels are used. [0013] Patent Literature 7 proposes a steel product for ballast tanks aiming at achieving maintenance free of vessels
- by improving corrosion resistance by adding Cr: 0.2 to 5 mass% as a corrosion-resistance improvement element to a steel containing C: 0.15 mass% or lower. Patent Literature 8 proposes a method for protecting ballast tanks from corrosion in which a steel product in which Cr: 0.2 to 5 mass% is added as a corrosion-resistance improvement element to a steel containing C: 0.15 mass% or lower is used as a constituent material and a ratio of the oxygen gas concentration in the ballast tank to the value in the atmosphere is adjusted to 0.5 or lower.
- [0014] Patent Literature 9 proposes achieving maintenance-free of corrosion protection of vessels by improving corrosion resistance by adding Cr: 0.5 to 3.5 mass% to a steel containing C: 0.1 mass% or lower. Patent Literature 10 discloses a steel product for vessels whose coating film damage resistance is improved by adding Ni: 0.1 to 4.0 mass% to a steel containing C: 0.001 to 0.025 mass% to thereby reduce maintenance expense, such as repair coating expense.
   [0015] Patent Literature 11 discloses a steel for vessels having corrosion resistance in the environment of an exterior plate, ballast tanks, cargo oil tanks, and a cargo hold for ore and coal of vessels by adding Cu: 0.01 to 2.00 mass% and Mg: 0.0002 to 0.0150 mass% to a steel containing C: 0.01 to 0.25 mass%.
- [0016] Patent Literature 12 or 13 discloses a steel product for cargo oil tanks whose resistance against general corrosion or local corrosion in a crude oil corrosion environment and a seawater corrosion environment by adding Cu: 0.05 to 2% and further compositely adding P, Ni, W, and Sn to a steel containing C: 0.01 to 0. 2% while suppressing the addition of Cr or Al.

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Citation List

Patent Literature

#### 40 [0017]

PTL 1: Japanese Unexamined Patent Application Publication No. 2003-082435
 PTL 2: Japanese Unexamined Patent Application Publication No. 2004-204344
 PTL 3: Japanese Unexamined Patent Application Publication No. Sho 48-050921
 PTL 4: Japanese Unexamined Patent Application Publication No. Sho 48-050922
 PTL 5: Japanese Unexamined Patent Application Publication No. Sho 48-050924
 PTL 6: Japanese Unexamined Patent Application Publication No. Hei 07-034197
 PTL 7: Japanese Unexamined Patent Application Publication No. Hei 07-034196
 PTL 8: Japanese Unexamined Patent Application Publication No. Hei 07-034270
 PTL 9: Japanese Unexamined Patent Application Publication No. Hei 07-310141
 PTL 10: Japanese Unexamined Patent Application Publication No. 2002-266052
 PTL 11: Japanese Unexamined Patent Application Publication No. 2000-017381
 PTL 12: Japanese Unexamined Patent Application Publication No. 2005-325439
 PTL 13: Japanese Unexamined Patent Application Publication No. 2007-270196

Summary of Invention

**Technical Problem** 

<sup>5</sup> [0018] As described above, in almost former cases, steel products for use in oil tanks of crude oil tankers and steel products for use in ballast tanks thereof have been separately developed. However, the back side of the bottom plate of oil tanks of tankers to be used in a no-coating state is usually also a ballast tank to be used with being coated. Therefore, the corrosion resistance in the corrosion environment in the oil tanks and the corrosion resistance in the corrosion environment of the ballast tanks cannot be separately considered as the characteristics to be imparted to steel products for use in tankers.

**[0019]** In contrast, the techniques described in Patent Literatures 12 and 13 aim at achieving both a crude oil corrosion environment and a seawater corrosion environment focusing on the fact that seawater is poured in the ballast tank disposed at the outside of a cargo oil tank when crude oil is not loaded. Then, with respect to the seawater corrosion environment, the corrosion resistance of the steel product itself is focused as corrosion resistance after a coating film

- of protecting coating of the external side of the cargo oil tank deteriorates. However, in the techniques, an improvement of the corrosion resistance in the state where a coating film is present is not considered at all. However, the improvement of the corrosion resistance in the state where a coating film is present on the surface of a steel product, which is not considered at all in the techniques of Patent Literatures 12 and 13, i.e., the corrosion resistance after coating, is very effective for extending the life of the corrosion-resistant steel product for crude oil tanker, and thus
- 20 the technical development thereof has been desired. However, in the actual condition, there is no technique for achieving the improvement.

**[0020]** Then, it is an object of the present invention to provide a corrosion-resistant steel product for tanker that is excellent in the corrosion resistance in the corrosion environment due to corrosive gas, such as  $H_2S$ , in the oil tanks of tankers and also excellent in the corrosion resistance after coating in the corrosion environment of the ballast tank.

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Solution to Problem

[0021] The present inventors have repeated extensive examination for developing a corrosion-resistant steel product for tanker having excellent corrosion resistance in the corrosion environment of both oil tanks and ballast tanks of tankers.
 <sup>30</sup> As a result, the present inventors have found that a corrosion-resistant steel product for tanker showing excellent corrosion environment in oil tanks and ballast tanks of tankers is obtained by blending Cr: more than 0.1 mass% and 0.5 mass% or lower and Cu: 0.03 to 0.5 mass% and, as an alternative addition element, one or two or more elements selected from W: 0.01 to 0.5 mass%, Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, Sb: 0.001 to 0.5 mass%, Ni: 0.005 to 0.3 mass%, and Co: 0.005 to 0.3 mass% and blending the components in such a manner as to satisfy a specific relationship. Then, the present invention has been accomplished.

- [0022] More specifically, the present invention is a corrosion-resistant steel product for crude oil tanker containing C: 0.03 to 0.16 mass%, Si: 0.05 to 1.50 mass%, Mn: 0.1 to 2.0 mass%, P: 0.025 mass% or lower, S: 0.01 mass% or lower, Al: 0.005 to 0.10 mass%, N: 0.008 mass% or lower, Cr: more than 0.1 mass% and 0.5 mass% or lower, and Cu: 0.03 to 0.5 mass% and, as an alternative addition element, one or two or more elements selected from W: 0.01 to 0.5 mass%,
- <sup>40</sup> Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, Sb: 0.001 to 0.5 mass%, Ni: 0.005 to 0.3 mass%, and Co: 0.005 to 0.3 mass%, so that the components satisfy that the X value defined by Equation (1);

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X value = 
$$(1 - 0.8 \times Cu^{0.3}) \times \{1 - (0.8 \times W + 0.4 \times Mo)^{0.3}\} \times \{1 - (0.8 \times Sn + 0.8 \times Sb)^{0.5}\} \times \{1 - (0.05 \times Cr + 0.03 \times Ni + 0.03 \times Co)^{0.3}\} \times (1 + S/0.01 + P/0.05)$$
 (1)

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is 0.5 or lower and the Y value defined by Equation (2):

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Y value = 
$$(1 - 0.3 \times Cr^{0.3}) \times \{1 - (0.8 \times W + 0.5 \times Mo)^{0.3}\} \times \{1 - (Sn + 0.4 \times Sb)^{0.3}\} \times \{1 - (0.1 \times Ni + 0.1 \times Co)^{0.3}\}$$

+ 0.05 × Cu)<sup>0.3</sup>} × {1 + (S/0.01 + P/0.08)<sup>0.3</sup>} (2)

<sup>5</sup> is 0.5 or lower, and the balance containing Fe and inevitable impurities. The element symbol of each equation represents the content (mass%) of each element.

**[0023]** The corrosion-resistant steel product for crude oil tanker of the invention contains one or two or more elements selected from W: 0.01 to 0.5 mass%, Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, and Sb: 0.001 to 0.5 mass% as the alternative addition element.

- [0024] The corrosion-resistant steel product for crude oil tanker of the invention contains one or two elements selected from Ni: 0.005 to 0.3 mass% and Co: 0.005 to 0.3 mass% in addition to the alternative addition elements.
   [0025] The corrosion-resistant steel product for crude oil tanker of the invention further contains one or two or more elements selected from Nb: 0.001 to 0.1 mass%, Ti: 0.001 to 0.1 mass%, Zr: 0.001 to 0.1 mass%, and V: 0.002 to 0.2
- mass% in addition to the component composition.
   [0026] The corrosion-resistant steel product for crude oil tanker of the invention further contains one or two or more elements selected from Ca: 0.0002 to 0.01 mass%, REM: 0.0002 to 0.015 mass%, and Y: 0.0001 to 0.1 mass% in addition to the component composition.

**[0027]** The corrosion-resistant steel product for crude oil tanker of the invention further contains B: 0.0002 to 0.003 mass% in addition to the component composition.

20 **[0028]** The corrosion-resistant steel product for crude oil tanker of the invention is obtained by forming a primer coating film containing Zn on the surface of the steel product.

**[0029]** The corrosion-resistant steel product for crude oil tanker of the invention is obtained by forming an epoxy type coating film on the surface of the steel product.

25 Advantageous Effects of Invention

**[0030]** The present invention can provide a steel product that is excellent in general corrosion resistance and local corrosion resistance in a corrosion environment of oil tanks of tankers in both a no-coating state or a state where zinc primer coating is performed or zinc primer coating and epoxy type coating are performed and also excellent in corrosion

<sup>30</sup> resistance after coating also in a corrosion environment of ballast tanks in a state where zinc primer coating is performed or zinc primer coating and epoxy type coating are performed. Accordingly, the steel product of the invention can be preferably used as materials constituting the oil tanks and the ballast tanks of tankers.

Brief Description of Drawings

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#### [0031]

[Fig. 1] Fig. 1 is a view of a test device used in a general corrosion test. [Fig. 2] Fig. 2 is a view of a test device used in a local corrosion test.

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### Description of Embodiments

**[0032]** The reasons for limiting the component composition of the steel product of the invention to the above-described range will be described.

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C: 0.03 to 0.16 mass%

**[0033]** C is an element effective for increasing the strength of steel and 0.03 mass% or more of C needs to be added in order to secure a desired strength in the invention. In contrast, the addition exceeding 0.16 mass% reduces the weldability and the toughness of a welded heat affected zone. Therefore, C is added in the range of 0.03 to 0.16 mass%. C is in the range of preferably 0.05 to 0.15 mass% and more preferably 0.10 to 0.15 mass%.

Si: 0.05 to 1.50 mass%

<sup>55</sup> **[0034]** Si is an element to be added as a deoxidizing agent and is also an element for increasing the strength of steel. In order to secure a desired strength, 0.05 mass% or more of Si is added in the invention. However, the addition exceeding 1.50 mass% reduces the toughness of steel. Therefore, Si is added in the range of 0.05 to 1.50 mass%. Si is in the range of preferably 0.20 to 1.50 mass% and more preferably 0.30 to 1.20 mass%.

Mn: 0.1 to 2.0 mass%

**[0035]** Mn is an element for increasing the strength of steel. In order to obtain a desired strength, 0.1 mass% or more of Mn is added in the invention. In contrast, the addition exceeding 2.0 mass% reduces the toughness and the weldability. Therefore, Mn is in the range of 0.1 to 2.0 mass%. Mn is added in the range of preferably 0.5 to 1.6 mass% and more preferably 0.7 to 1.5 mass%.

P: 0.025 mass% or lower

- <sup>10</sup> **[0036]** P is a harmful element that segregates in the grain boundary to reduce the toughness of steel, and thus the P content is preferably reduced as much as possible. In particular, when P is blended exceeding 0.025 mass%, the toughness considerably decreases. When the P content exceeds 0.025 mass%, the corrosion resistance is also adversely affected. Therefore, the P content is in the range of 0.025 mass% or lower. The P content is preferably 0.015 mass% or lower and more preferably 0.008 mass% or lower.
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S: 0.01 mass% or lower

**[0037]** S is a harmful element that forms MnS which is a non-metal inclusion to become a starting point of local corrosion to reduce the local corrosion resistance. Thus, the S content is reduced as much as possible. In particular, the content exceeding 0.01 mass% causes remarkable reduction in the local corrosion resistance. Therefore, the upper limit of S is 0.01 mass%. The upper limit is preferably 0.005 mass% or lower and more preferably 0.001 mass% or lower.

AI: 0.005 to 0.10 mass%

<sup>25</sup> **[0038]** Al is an element to be added as a deoxidizing agent and needs to be added in a proportion of 0.005 mass% or more in the invention. However, the addition exceeding 0.10 mass% reduces the toughness of steel. Thus, the upper limit of Al is 0.10 mass%. The upper limit is preferably 0.01 to 0.06 mass% and more preferably 0.02 to 0.05 mass%.

N: 0.008 mass% or lower

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**[0039]** N is a harmful element that reduces the toughness and thus the content thereof is reduced as much as possible. In particular, the addition exceeding 0.008 mass% considerably reduces the toughness. Thus, the upper limit is 0.008 mass%. The upper limit is preferably 0.005 mass% or lower and more preferably 0.004 mass% or lower.

<sup>35</sup> Cr: More than 0.1 mass% and 0.5 mass% or lower

**[0040]** Cr shifts into a rust layer with progress of corrosion to block the entry of Cl<sup>-</sup> into the rust layer, thereby suppressing concentration of Cl<sup>-</sup> to the interface of the rust layer and a base metal. When a Zn containing primer is applied, a complex oxide of mainly Fe and Cr or Zn is formed, and Zn can be present on the surface of a steel plate over a long period of time. Thus, the corrosion resistance can be sharply improved. In particular, the above-described effect is effective for improving the corrosion resistance in an environment in contact with seawater containing a salt, such as in ballast tanks serving as the back side of the bottom plate of oil tanks of tankers. By performing Zn containing primer treatment to a steel product containing Cr, the corrosion resistance can be sharply improved compared with a steel product not containing Cr. The above-described effect of Cr is not sufficiently obtained when the Cr content is 0.1 mass% or lower.

<sup>45</sup> However, in contrast, the addition exceeding 0.5 mass% reduces the toughness of a welding portion. Therefore, the Cr content is in the range of more than 0.1 mass% and 0.5 mass% or lower. In particular, when a favorable welding portion toughness is required, the Cr amount is preferably 0.11 to 0.20 mass% and more preferably 0.11 to 0.16 mass%.

Cu: 0.03 to 0.5 mass%

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**[0041]** Cu is an element for increasing the strength of steel, and is present in rust generated by corrosion of steel and has an effect of improving corrosion resistance. These effects are not sufficiently obtained when added in a proportion of lower than 0.03 mass%. In contrast, the addition exceeding 0.5 mass% has a possibility of causing a reduction in the toughness of a welded heat affected zone, surface cracking during manufacturing, etc. Therefore, Cu is added in the range of 0.03 to 0.5 mass%. Cu is preferably 0.04 to 0.20 mass% and more preferably 0.04 to 0.15 mass%.

**[0042]** The steel product of the invention needs to contain one or two or more elements selected from W, Mo, Sn, Sb, Ni, and Co as an alternative addition element in addition to the components described above.

W:0.01 to 0.5 mass%

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**[0043]** W has an effect of suppressing pitting corrosion in the bottom plate of oil tanks of tankers and also has an effect of increasing the corrosion resistance against general corrosion of an upper deck of tankers or corrosion resistance after coating in a corrosion environment in which immersion in salt water and a high moistness state is repeated, such as in ballast tanks. The above-described effect is developed by the addition of 0.01 mass% or more. However, the effect is saturated when the content exceeds 0.5 mass%. Thus, W is added in the range of 0.01 to 0.5 mass%. The content is preferably in the range of 0.02 to 0.3 mass%. The content is more preferably in the range of 0.03 to 0.10 mass%.

- **[0044]** The reason why W has the effect of improving the corrosion resistance as described above is considered to reside in that  $WO_4^{2-}$  generates in rust generated with corrosion of a steel plate, and the  $WO_4^{2-}$  suppresses the entry of chloride ion into the surface of the steel plate. It is also considered that  $FeWO_4$  generate in a portion where the pH decreases, such as in an anode section on the surface of the steel plate, and the  $FeWO_4$  also suppresses the entry of chloride ion into the surface of the steel plate, and as a result the corrosion of the steel plate is effectively suppressed. Furthermore, it is considered that the inhibiting action obtained by adsorption of  $WO_4^{2-}$  to the surface of a steel product
- <sup>15</sup> suppresses the corrosion of the steel.

Mo: 0.01 to 0.5 mass%

- [0045] Mo has effects of not only suppressing the pitting corrosion in the bottom plate of oil tanks of tankers but increasing the corrosion resistance against general corrosion of an upper deck of tankers or the corrosion resistance after coating in a corrosion environment in which salt water immersion and a high moistness state are repeated, such as in ballast tanks. The above-described effects are developed when Mo is added in a proportion of 0.01 mass% or more but the effects are saturated when added exceeding 0.5 mass%. Therefore, Mo is added in the range of 0.01 to 0.5 mass%. The content is preferably in the range of 0.03 to 0.4 mass%. The content is more preferably in the range
- <sup>25</sup> of 0.03 to 0.10 mass%.

The reason why Mo has the effect of improving the corrosion resistance as described above is considered to reside in that  $MoO_4^{2-}$  generated in rust generated with the corrosion of a steel plate similarly as W, and the  $MoO_4^{2-}$  suppresses the entry of chloride ion into the surface of the steel plate, and as a result the corrosion of the steel plate is effectively suppressed.

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Sn:0.001 to 0.2 mass%, Sb: 0.001 to 0.5 mass%

[0046] Sn and Sb have effects of not only suppressing pitting corrosion in the bottom plate of oil tanks of tankers but increasing corrosion resistance against general corrosion of an upper deck of tankers or corrosion resistance after coating in a corrosion environment in which salt water immersion and a high moistness state are repeated, such as in ballast tanks. The above-described effects are developed by adding Sn: 0.001 mass% or more and Sb: 0.001 mass% or more. In contrast, even when Sn: more than 0.2 mass% and Sb: more than 0.5 mass% are added, the effects are merely saturated. Therefore, Sn is added in the range of 0.001 to 0.2 mass% and Sb is added in the range of 0.001 to 0.5 mass%. Sn is preferably 0.005 to 0.10 mass%.

Ni: 0.005 to 0.3 mass%, Co: 0.005 to 0.3 mass%

- [0047] By generating fine rust particles, Ni and Co have an effect of improving the corrosion resistance in a no-coating
   state and the corrosion resistance in a state where an epoxy type coating is performed to a zinc primer coating film to
   no small extent. Therefore, these elements are preferably blended for further improving the corrosion resistance. The
   above-described effect is developed by the addition of Ni: 0.005 mass% or more and Co: 0.005 mass% or more. In
   contrast, even when Ni: more than 0.3 mass% and Co: more than 0.3 mass% are added, the effect is saturated. Therefore,
   Ni and Co are preferably added in the above-described ranges. Ni is preferably 0.01 to 0.2 mass% and more preferably
   0.03 to 0.15 mass%. Co is preferably 0.01 to 0.2 mass% and more preferably 0.03 to 0.15 mass%.
- [0048] It is necessary for the steel product of the invention that the above-described components are contained in the proper ranges and also that the components are contained satisfying that the X value defined by Equation (1) is 0.5 or lower and the Y value defined by Equation (2) is 0.5 or lower:

X value =  $(1 - 0.8 \times Cu^{0.5}) \times \{1 - (0.8 \times W + 0.4 \times Mo)^{0.3}\} \times \{1 - (0.8 \times Sn + 0.8 \times Sb)^{0.5}\} \times \{1 - (0.05 \times Cr + 0.03 \times Ni + 0.03 \times Co)^{0.3}\} \times (1 + S/0.01 + P/0.05)$  (1),

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Y value =  $(1 - 0.3 \times Cr^{0.3}) \times \{1 - (0.8 \times W + 0.5 \times Mo)^{0.3}\} \times \{1 - (Sn + 0.4 \times Sb)^{0.3}\} \times \{1 - (0.1 \times Ni + 0.1 \times Co + 0.05 \times Cu)^{0.3}\} \times \{1 + (S/0.01 + P/0.08)^{0.3}\}$  (2).

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The element symbol of each equation represents the content (mass%) of each element.

- [0049] Here, Equation (1) above is an equation for evaluating the influence of each component exerted on the corrosion in oil tanks of tankers and the coefficient of the components for increasing the corrosion resistance is represented as minus and the coefficient of the components deteriorating the corrosion resistance is represented as plus. Therefore, steel products having a smaller X value are excellent in corrosion resistance. The present inventors have investigated the relationship between the X value and the corrosion resistance of the steel products in a corrosion environment in oil tanks of tankers. As a result, the present inventors have found that when X is 0.5 or lower, the corrosion resistance
- <sup>25</sup> in the corrosion environment in oil tanks of tankers is excellent but when X exceeds 0.5, the corrosion resistance is poor. Thus, the steel products of the invention need to blend components so that the X value is 0.5 or lower. The X value is more preferably 0.4 or lower.

**[0050]** Equation (2) above is an equation for evaluating the influence of each component exerted on the corrosion resistance after coating of ballast tanks. Similarly as in Equation (1) above, the coefficient of the components for increasing

- 30 the corrosion resistance is represented as minus and the coefficient of the components deteriorating the corrosion resistance is represented as plus. Therefore, steel products having a smaller Y value are excellent in corrosion resistance. The present inventors have investigated the relationship between the Y value and the corrosion resistance after coating of the steel products in the corrosion environment in ballast tanks. As a result, the present inventors have found that when Y is 0.5 or lower, the corrosion resistance after coating in the corrosion environment in ballast tanks is excellent
- <sup>35</sup> but when Y exceeds 0.5, the corrosion resistance is poor. Thus, the steel products of the invention need to blend components so that the Y value is 0.5 or lower. The Y value is more preferably 0.4 or lower.
   [0051] In order to effectively develop, with a small number of elements to be added, the effects of suppressing the pitting corrosion in the bottom plate of oil tanks of tankers and the general corrosion in an upper deck of tankers and increasing the corrosion resistance after coating in the corrosion environment in which salt water immersion and a high
- 40 moistness state are repeated, such as in ballast tanks, the steel product of the invention preferably contains one or two or more elements selected particularly from W: 0.01 to 1.0 mass%, Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, and Sb: 0.001 to 0.5 mass% among the above-described alternative addition elements, and secondly preferably contains one or two or more elements selected from Ni and Co.
- [0052] The steel product of the invention can contain one or two or more elements selected from Nb, Ti, Zr, and V in the following ranges in addition to the above-described components in order to increase the strength of steel. Nb: 0.001 to 0.1 mass%, Ti:0.001 to 0.1 mass%, Zr: 0.001 to 0.1 mass%, V: 0.002 to 0.2 mass%
  Nb, Ti, Zr, and V each are elements having an effect of increasing the strength of steel products, and can be selected and added according to a required strength. In order to obtain the above-described effects, it is preferable that Nb, Ti, and Zr be added in a proportion of 0.001 mass% or more and V be added in a proportion of 0.002 mass% or more.
- <sup>50</sup> However, when Nb, Ti, and Zr are added in a proportion of more than 0.1 mass% and V is added in a proportion of more than 0.2 mass%, the toughness decreases. Thus, Nb, Ti, Zr, add V are preferably added in the above-described ranges. Nb is preferably 0.004 to 0.05 mass% and more preferably 0.005 to 0.02 mass%. Ti is preferably 0.002 to 0.03 mass% and more preferably 0.001 to 0.05 mass% and more preferably 0.002 to 0.01 mass%. Zr is preferably 0.001 to 0.05 mass% and more preferably 0.002 to 0.01 mass%. V is preferably 0.003 to 0.15 mass% and more preferably 0.004 to 0.1 mass%.
- <sup>55</sup> **[0053]** In order to increase the strength or increase the toughness, the steel product of the invention can contain one or two or more elements selected from Ca, REM, and Y in the following ranges in addition to the above-described components.

Ca: 0.0002 to 0.01 mass%, REM: 0.0002 to 0.015 mass%, and Y: 0.0001 to 0.1 mass%

**[0054]** Ca, REM, and Y each have an effect of improving the toughness of a welded heat affected zone, and can be added as required. The above-described effects are obtained by adding Ca: 0.0002 mass% or more, REM: 0.0002 mass% or more, and Y: 0.0001 mass% or more. However, Ca: more than 0.01 mass%, REM: more than 0.015 mass%, and Y: more than 0.1 mass% are added, the toughness decreases on the contrary. Thus, Ca, REM, and Y are preferably in the above-described ranges. Ca is preferably 0.001 to 0.005 mass% and more preferably 0.001 to 0.001 to 0.003 mass%. REM is preferably 0.0005 to 0.015 mass% and more preferably 0.001 to 0.010 mass%. Y is preferably 0.0001 to 0.05 mass% and more preferably 0.0002 to 0.01 mass%.

<sup>10</sup> **[0055]** Furthermore, the steel product of the invention can further contain B in the following range in addition to the above-described components.

#### B: 0.0002 to 0.003 mass%

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- <sup>15</sup> **[0056]** B is an element for increasing the strength of the steel products and can be added as required. In order to obtain the above-described effect, 0.0002 mass% or more of B is preferably added. However, B is added exceeding 0.003 mass%, the toughness decreases. Therefore, B is preferably added in the range of 0.0002 to 0.003 mass%. B is preferably 0.0002 to 0.002 mass% and more preferably 0.0002 to 0.0015 mass%.
- The steel product for tankers of the invention manufactured by the above-described method using a steel base material having the above-described component composition has a feature in that the steel product for tankers of the invention is excellent not only in the corrosion resistance (general corrosion resistance, local corrosion resistance) in no-coating state but in the corrosion resistance after coating. In particular, the steel product for crude oil tanks of the invention can sharply improve the local corrosion resistance and general corrosion resistance by forming a zinc primer coating film while adjusting the coating amount of a coating, such as a primer containing a metal Zn or a Zn compound (hereinafter
- <sup>25</sup> collectively referred to as a "zinc primer") to 1.0 g/m<sup>2</sup> or more in terms of Zn content. The coating amount is preferably 10 g/m<sup>2</sup> or more in terms of average Zn content. The coating amount is more preferably 15 g/m<sup>2</sup> or more. The relationship between the coating film thickness of the zinc primer and the Zn content of the surface of the steel product depends on the Zn content in the zinc primer. In general, when the thickness is 10  $\mu$ m or more in terms of average coating thickness, the entire surface of the steel product can be covered. Irrespective of the kind of the zinc primer, the coating amount of
- <sup>30</sup> at least 1.0 g/m<sup>2</sup> or more can be secured. From the viewpoint of increasing the corrosion resistance, the upper limit of the film thickness of the zinc primer is not particularly determined. However, when the coating film becomes thick, the cutting properties or weldability decreases. Thus, cutting or welding is performed after applying the zinc primer, the film thickness of the zinc primer is preferably 100 µm or lower and more preferably 50 µm or lower. Such zinc primer coating may be performed, for example, after performing shotblasting treatment to the surface of the steel product.
- The steel product for crude oil tanks of the invention can form an epoxy type coating film by applying an epoxy type paint or the like on a no-coating steel product surface or a steel product surface after the application of the zinc primer. Thus, the local corrosion resistance and general corrosion resistance can be further improved as compared with the case of former steel products for vessels and also, particularly when used for ballast tanks or the like under a severe corrosion environment due to seawater, an effect of improving a more preferable corrosion resistance after coating, for example, coating film swelling resistance, is obtained.
- Here, the epoxy type coating film is not particularly limited, and various kinds of epoxy type resin can be used. For example, a modified epoxy resin, a tar epoxy resin, and the like can be used. The film thickness of the epoxy type coating film is not particularly limited, and is preferably 500 μm or lower and more preferably 350 μm or lower from the viewpoint of coating cost or workability and can be selected as appropriate according to required properties.
- 45

#### EXAMPLES

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**[0057]** Various kinds of steel having component compositions of No. 1 to No. 36 shown in Table 1 are melted in a vacuum melting furnace or a converter to form steel slabs. The steel slabs are reheated to 1200°C, and subjected to hot rolling at a finishing temperature of 800°C, thereby obtaining steel plates having a plate thickness of 16 mm. The steel plates thus obtained of No. 1 to No. 36 were subjected to the following three kinds of corrosion resistance tests.

(1) General corrosion test in which an environment of an upper deck of a tanker was simulated

<sup>55</sup> **[0058]** In order to evaluate the corrosion resistance against general corrosion in the back side of an upper deck of a tanker, small rectangular pieces of Width 25 mm × Length 48 mm × Thickness 4 mm were cut out from the thick steel plates of No.1 to No. 36, and then the surface thereof was subjected to shotblasting to obtain no-coating corrosion coupons. Then, a general corrosion test was performed using corrosion test equipment shown in Fig. 1. The corrosion

test equipment is constituted by a corrosion test chamber 2 and a temperature-controlled plate 3. In the corrosion test chamber 2, water 6 whose temperature was held at 40°C was poured and, to the water 6, a mixed gas containing 12 vol% CO<sub>2</sub>, 5 vol% O<sub>2</sub>, 0.01 vol% SO<sub>2</sub>, 0.3 vol% H<sub>2</sub>S, and the balance N<sub>2</sub> (introduced gas 4) was introduced, so that the inside of the corrosion test chamber 2 was filled with supersaturated vapor, thereby reproducing the corrosion environment

- of the back side of an upper deck of crude oil tanks. Then, a corrosion coupon 1 placed on the upper back side of the test chamber was repeatedly subjected to temperature changes for 180 days in one cycle of 30°C × 4 hours + 50°C × 4 hours through the temperature-controlled plate 3 containing a heater and a cooling system to generate dew condensation water on the surface of the coupon 1, thereby causing general corrosion. In Fig. 1, the reference numeral 5 represents emission gas from the test chamber.
- 10 [0059] After the test, a reduction in the plate thickness due to corrosion was determined from the mass changes before and after the test about each the coupon. When the case where the reduction in the plate thickness was 60% or lower to the value of a comparative steel of No. 36 was evaluated that the general corrosion resistance was very good (☉), the case where the reduction is more than 60% and 70% or lower was evaluated that the general corrosion resistance was good (☉), and the case where the reduction is more than 70% was evaluated that the general corrosion resistance
- <sup>15</sup> was poor (x).

(2) Pitting corrosion test in which an environment of the bottom plate of oil tanks of a tanker was simulated

 $\begin{bmatrix} 0060 \end{bmatrix} \quad \text{From the same steel plates of No. 1 to No. 36 used in the test of (1), small square pieces of Width 50 mm $\times$ Length 50 mm $\times$ Thickness 15 mm were cut out, the surface thereof was subjected to shotblasting, and then an inorganic system zinc primer was separately applied with two levels of a coating film thickness of 0 micrometer (no coating) and 15 to 25 $\mu$m. }$ 

Subsequently, the end sides and the back side of the four kinds of coupons were subjected to masking with a corrosion protecting paint, and then a sludge containing crude oil components extracted from an actual tanker was applied to the

- right face serving as a side to be subjected to the corrosion test, thereby obtaining corrosion coupons. In the test, a sulfur mixed sludge in which 50 mass% of sulfur was mixed with the sludge was applied to a 2 mm

  portion of the test target side and only the sludge was uniformly applied to other portions. With the coupons, the portion to which the sulfur mixed sludge was applied became a starting point of corrosion and promoted local corrosion. Thus, the influence of the steel product components, the primer, and the combination thereof affecting suppression of the local corrosion can be further accurately understood.
- <sup>30</sup> corrosion can be further accurately understood.
  [0061] These coupons were then subjected to a corrosion test in which the coupons were immersed for one month in a test liquid 12 of corrosion test equipment shown in Fig. 2. The corrosion test equipment is double-type equipment containing a corrosion test chamber 8 and a constant-temperature bath 9. In the corrosion test chamber 8, a test liquid 12 capable of causing the same local corrosion as that generating in the bottom plate of an actual oil tank was put, and
- a coupon 7 was immersed therein. Used as the test liquid 12 was a liquid containing artificial seawater specified in ASTM D1141 as a test mother water, into which a mixed gas (introduced gas 10) in which the partial pressure ratio was adjusted to 5 vol% O<sub>2</sub> + 10 vol% H<sub>2</sub>S and which contained the balance N<sub>2</sub> gas was introduced. The temperature of the test liquid 12 was held at 50°C by adjusting the temperature of the water 13 put into the constant-temperature bath 9. Since the introduced gas 10 was continuously supplied, the test liquid 12 was always stirred. In Fig. 2, the reference numeral 11
   represents emission gas from the test chamber.
- **[0062]** After the corrosion test, rust generated on the coupon surface was removed, and then the corrosion state was visually observed and also the corrosion depth of a local corrosion generating portion was measured by a depth meter. The case where the corrosion depth was 40% or lower to the value of the comparative steel of No.36 was evaluated that the local corrosion resistance was very good ( $\odot$ ), the case where the corrosion depth was more than 40% and 50%
- or lower was evaluated that the local corrosion resistance was good (O), and the case where the corrosion depth was more than 50% was evaluated that the local corrosion resistance was poor ( $\times$ ).

(3) Corrosion after coating test in which a ballast tank environment was simulated

- <sup>50</sup> **[0063]** In order to evaluate the corrosion resistance after coating in a ballast tank environment, from the same steel plates of No. 1 to No. 36 used in the test (1), coupons of Width 50 mm × Length 150 mm × Thickness 5 mm were collected. Then, the surface of the coupons was subjected to shotblasting, and then subjected to surface treatment of the following conditions A and B, thereby producing exposed coupons:
- <sup>55</sup> Conditions A: Formation of a two-layer coating film of a zinc primer (about 15  $\mu$ m) and a tar epoxy resin paint (about 200  $\mu$ m) on the coupon surface,

Conditions B: Formation of a single-layer coating film of a tar epoxy resin paint (about 200  $\mu$ m) on the coupon surface.

To the coupons having a coating film in the conditions A and B, a 80 mm length scratch reaching the surface of a base metal was given in a straight line with a utility knife from the top of the coating film.

Thereafter, these coupons were subjected to a corrosion test in which one cycle of (held in artificial seawater having a temperature of  $30^{\circ}$ C for 1 day)  $\rightarrow$  (held in a wet atmosphere having a relative humidity of 98 to 99% at a temperature of  $40^{\circ}$ C for 1 day)  $\rightarrow$  (held in a wet atmosphere having a relative humidity of 98 to 99% at a temperature of  $40^{\circ}$ C for 1 day) are repeated by C0 avalage (for 120 days) are corrected by C0 avalage (for 120 days).

- of 40°C for 1 day) was repeated by 60 cycles (for 120 days) as a corrosion cycle test in which the environment of a ballast tank of an actual ship was simulated. The corrosion resistance of each coupon was evaluated as follows. The coupons having a coating film in the conditions A and B were measured for the coating film swelled area generated around the scratch. Then the case where the area ratio was 50% or lower to the value of the comparative steel of No. 36 was evaluated that the corrosion resistance after coating was very good ((()), the case where the area ratio was more
- 10 than 50% and 70% or lower was evaluated that the corrosion resistance after coating was good (O), and the case where the area ratio was more than 70% was evaluated that the corrosion resistance after coating was poor (x).
  [0064] The corrosion resistance test results of (1) to (3) were shown in Table 2 with the X values and the Y values determined from the component composition of each steel plate. Table 2 shows that the thick steel plates of No. 1 to No. 30 satisfying the component composition of the invention and the conditions of the X value and the Y value exhibit
- excellent corrosion resistance higher than a target level as a ratio to a base steel product (No. 36) in all the corrosion tests of (1) to (3) and, in contrast, corrosion exceeding a target level as a ratio to the steel product of No. 36 is observed in the thick steel plates of No. 31 to No. 35 not satisfying the conditions of the invention in any one or more of the corrosion tests.
- 20 Industrial Applicability

**[0065]** The steel product of the present invention can be preferably used not only in crude oil tankers but also crude oil tanks of other vessels and crude oil tanks used on the ground, for example.

25 Reference Signs List

#### [0066]

- 1, 7 Coupon
  - 2, 8 Corrosion test chamber
  - 3 Temperature-controlled plate
  - 4, 10 Introduced gas
  - 5, 11 Emission gas
  - 6, 13 Water
- 35 9 Constant temperature bath
  - 12 Test liquid

[Table 1-1]

40 [0067]

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present inveniton Steel of present inveniton Steel of present inveniton Steel of present inveniton Steel of present inveniton present inveniton Steel of present inveniton Steel of present inveniton Steel of Steel of Remarks 5 X value Y value 0.35 0.38 0.39 0.39 0.45 0.33 0.44 0.41 0.30 0.32 0.43 0.33 0.22 0.32 0.44 0.31 10 Nb, Ti, V, Zr,Ca, REM,Y, B Zr:0.006 Ti:0.003 REM: 0.002 Nb: 0.015 ı ı ı ı 15 ပိ ī ı ī ı ı ī ī ī 0.15 0.09 ï ı ı ī ī ī ī 20 0.15 0.05 0.10 0.02 0.03 Sb ī ī ı 0.03 0.08 0.05 0.20 S ı ī ı ı 25 0.03 0.30 ۶ 0.1 ī ı ī ı ī 0.05 0.05 0.05 0.20 Table 1-1 ≥ ı ı ī ı Chemical components (mass%) 30 0.08 0.10 0.06 0.06 0.50 0.06 0.10 0.06 5 0.13 0.13 0.40 0.13 0.13 0.13 0.15 0.13 ັບ 35 0.003 0.002 0.002 0.002 0.003 0.003 0.002 0.002 z 0.033 0.029 0.026 0.035 0.028 0.025 0.033 0.031 ₹ 40 0.0004 0.0060 0.0004 0.0007 0.0004 0.0004 0.0004 0.0004 S 45 0.015 0.007 0.007 0.007 0.007 0.007 0.007 0.007 ۲ 1.58 1.61 1.78 1.25 1.32 1.4 1 1.46 1.22 Ę 50 0.35 0.34 0.32 0.31 0.33 0.30 0.34 0.34 ŝ 0.03 0.06 0.06 0.06 0.03 0.03 0.06 0.06 C 55 Steel Ś 2 ო 4 S ശ  $\sim$ <del>.</del> ∞

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present inveniton Steel of present inveniton present inveniton present inveniton Steel of Steel of Steel of Remarks 5 X value Y value 0.45 0.48 0.39 0.43 0.45 0.42 0.41 0.44 0.27 0.23 0.35 0.39 0.38 0.37 0.38 0.38 10 Nb,Ti, V, Zr,Ca, REM,Y, Ca: 0.0016 Ca: 0.0016 Y:0.01 Nb: 0.015 ш ı ı ı ı 15 0.3 ပိ ī ı ı ī ı ı. ı 0.03 0.30 0.01 ī ī ı ı ı ı 20 0.10 0.05 0.05 0.05 0.50 Sb ī ï ı 0.03 0.03 0.01 S ı ī ī ı ı. 25 0.05 0.02 0.05 0.01 ٩ ı ī ı ı 0.05 0.05 0.05 0.05 0.01 (continued) Chemical components (mass%) ≥ ı ı ı 30 0.06 0.10 0.06 0.06 0.06 0.06 0.06 0.50 5 0.13 0.45 0.13 0.13 0.13 0.13 0.13 0.13 ັບ 35 0.002 0.003 0.002 0.003 0.003 0.002 0.003 0.003 z 0.032 0.028 0.034 0.034 0.028 0.031 0.031 0.031 ₹ 40 0.0015 0.0003 0.0010 0.0004 0.0004 0.0004 0.0004 0.0004 S 45 0.003 0.007 0.003 0.007 0.007 0.007 0.007 0.007 ۲ 1.60 1.51 1.16 1.35 1.23 1.29 1.34 1.51 ЫЧ 50 0.35 0.33 0.33 0.32 0.33 0.32 0.32 0.33 ŝ 0.06 0.08 0.08 0.06 0.08 0.08 0.08 0.11 C 55 Steel 2 <u>5</u> 5 9 . Р 9 4 ი ÷

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_		Co Zr,Ca, Zr,Ca, B Y value Remarks B B	Steel of present inveniton	Steel of present inveniton
5		Y value	0.39	0.40
10		X value	0.32	0.39
		Nb,Ti, V, Zr,Ca, REM,Y, B	Ti:0.003	
15		ပိ	1	I
		Ē	1	1
20		Sb	0.10	I
		Ŋ	1	0.05
25		Mo		ı
00 (continued)	ss%)	>	0.06	0.06
(contir	ents (ma	Cu	0.06	0.04
35	sompone	ර්	0.003 0.13	0.13
	Chemical components (mass%)	z	0.003	0.003
40	U	А	0.029	0.034
45		w	0.0004	0.0010
70		۵	0.007	0.007
50		ЧМ	0.34 1.07	1.12
		ō	0.34	0.33
55		U	0.11	0.11
	Steel	No.	17	18

[Table 1-2]

# [0068]

5		Remarks	Steel of present invention							
		Y value	0.42	0.38	0.4	0.36	0.36	0.4	0.37	0.37
10		X value Y value	0.42	0.25	0.27	0.33	0.29	0.31	0.26	0.31
15		Nb,Ti, V, Zr,Ca, REM,Y, B	V:0.03	I	I	I	I	B: 0.0011	Nb: 0.008, Zr:0.006	ı
		ပိ				ı	0.10	ı		
20		Ż	ı	0.15	0.20	0.05	ı	ı	ı	,
		Sb	ı	0.01	0.01	0.05	ı	0.02	ı	0.05
25		Sn	0.05	ı	ı	0.03	ı	ı	ı	ı
30 dar - L adar	- (%)	Mo	I	I	ı	I	0.40	0.05	ı	0.20
30 49 E	Chemical components (mass%)	3	0.06	0.06	0.06	0.05	I	0.10	0.30	ı
35	nponen	Cu	0.04	0.30	0.40	0.08	0.08	0.08	0.06	0.06
	nical co	ت	0.13	0.50	0.30	0.11	0.13	0.11	0.13	0.13
40	Cher	z	0.003	0.002	0.003	0.003	0.002	0.002	0.002	0.002
		А	0.034	0.025	0.032	0.029	0.034	0.029	0.033	0.028
45		S	0.0020	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
		٩	0.007	0.010	0.020	0.007	0.007	0.007	0.007	0.007
50		Mn	1.25	1.13	1.28	1.05	1.10	1.18	0.97	1.02
		ũ	0.31	0.34	0.32	0.34	0.31	0.35	0.30	0.35
55		U	0.11	0.11	0.11	0.13	0.13	0.13	0.13	0.16
	Steel	No.	19	20	21	22	23	24	25	26

5		Remarks	Steel of present invention	Steel of present invention	Steel of present invention	Steel of present invention	Comparative steel	Comparative steel	Comparative steel	Comparative steel	Comparative steel	Comparative steel
		Y value	0.39	0.39	0.39	0.36	0.52	0.44	0.45	0.67	0.72	1.66
10		X value	0.41	0.34	0.25	0.21	0.52	0.55	0.54	0.56	0.50	1.34
15		Nb,Ti, V, Zr,Ca, REM,Y, B	V:0.03	ı	ı	REM: 0.002	ı	ı	ı	ı	ı	ı
		ပိ	ı	ı.	ı	ı	ı	T	T	0.01	I	I
20		Ē	ı	0.10	0.10	I	ı	0.03	I	0.01	0.10	ı
		ß	·	0.03		0.08	0.05	0.10	0.05	0.001	ı	ı
25		Sn	0.12	I	I	ı	0.03	0.03	I	0.001	I	ı
(continued)	ý (%;	Mo	I	0.08	I	0.10	0.05	I	0.20	0.01	0.05	I
30 (conti	ts (mass	>	0.01	0.02	0.20	I	ı	0.05	I	0.01	I	I
35	nponen	C	0.04	0.10	0.20	0.50	0.00	0.35	0.06	0.03	0.40	I
	Chemical components (mass%)	స	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.11	0.08	I
40	Cher	z	0.002	0.003	0.002	0.003	0.002	0.002	0.003	0.003	0.002	0.002
		P	0.028	0.032	0.033	0.035	0.030	0.027	0.033	0.033	0.033	0.032
45		٥	0.0004	0.0004	0.0008	0.0020	0.0020	0.0200	0.0004	0.0004	0.0060	0.0010
		٩	0.007	0.007	0.007	0.007	0.007	0.012	0.050	0.007	0.015	0.012
50		ЧW	0.96	66.0	1.11	1.08	1.76	1.36	1.25	1.19	1.18	1.23
		<u>ت</u>	0.30	0.33	0.32	0.34	0.34	0.31	0.30	0.32	0.32	0.32
55		ပ	0.16	0.16	0.16	0.16	0.03	0.06	0.08	0.11	0.13	0.11
	Steel	No.	27	28	29	30	31	32	33	34	35	36

# [Table 2]

# [0069]

5	Table 2							
	Steel General corrosion		Evaluation	n of pitting	Evaluation of ballast tank	f corrosion in environment	Overall evaluation	
10	No.	resistance on back side of upper deck	corrosion resitance on bottom plate of oik tank		Corrosion test i of salt water ir high moist	mmersion and		Remarks
15		No-coating state	No-coating state	Zn primer	Zn primer + Resin coating	Resin coating		
	1	۵	۵	۵	۵	۵	Ø	Steel of present invention
20	2	0	0	0	0	0	0	Steel of present invention
25	3	0	0	0	Ø	0	0	Steel of present invention
	4	Ø	Ø	Ø	Ø	Ø	Ø	Steel of present invention
30	5	Ø	Ø	ø	Ø	Ø	Ø	Steel of present invention
35	6	Ø	Ø	ø	0	0	0	Steel of present invention
	7	Ø	Ø	ø	0	0	0	Steel of present invention
40	8	0	0	0	0	0	0	Steel of present invention
45	9	Ø	Ø	Ø	0	0	0	Steel of present invention
50	10	0	0	Ø	0	0	0	Steel of present invention
50	11	۵	۵	۵	۵	۵	Ø	Steel of present invention
55	12	۵	Ø	Ø	0	0	0	Steel of present invention

	Steel	General corrosion	Evaluation of pitting		Evaluation of ballast tank		Overall evaluation	
5	No.	resistance on back side of upper deck	corrosion r	esitance on e of oik tank	Corrosion test i of salt water ir high moist	nmersion and		Remarks
10		No-coating state	No-coating state	Zn primer	Zn primer + Resin coating	Resin coating		
15	13	۲	۲	۲	0	0	0	Steel of present invention
	14	۵	0	0	0	0	0	Steel of present invention
20	15	۵	۵	ø	0	0	0	Steel of present invention
25	16	۵	۲	۵	0	0	0	Steel of present invention
	17	۵	۲	۲	۲	۵	Ø	Steel of present invention
30	18	۵	۲	۲	0	0	0	Steel of present invention
35	19	0	0	0	0	0	0	Steel of present invention
	20	0	0	۲	۲	0	0	Steel of present invention
40	21	0	0	۲	0	0	0	Steel of present invention
45	22	Ø	۵	Ø	۵	Ø	Ø	Steel of present invention
	23	0	0	0	0	0	0	Steel of present invention
50	24	0	0	0	0	0	0	Steel of present invention
55	25	Ø	Ø	Ø	0	0	0	Steel of present invention

(continued)

				(0	continued)				
	Steel	General corrosion	Evaluation of pitting		Evaluation of ballast tank		Overall evaluation		
5	No.	resistance on back side of upper deck	corrosion r	esitance on e of oik tank	Corrosion test i of salt water ir high moist	nmersion and		Remarks	
10		No-coating state	No-coating state	Zn primer	Zn primer + Resin coating	Resin coating			
15	26	۲	۵	Ø	۲	۵	0	Steel of present invention	
	27	0	۲	0	0	0	0	Steel of present invention	
20	28	۵	۲	۲	۲	O	0	Steel of present invention	
25	29	0	0	0	0	0	0	Steel of present invention	
	30	۲	۲	۲	۲	۵	0	Steel of present invention	
30	31	×	×	×	×	×	×	Comparative steel	
	32	×	×	×	0	0	×	Comparative steel	
35	33	×	×	×	0	0	×	Comparative steel	
	34	×	×	×	×	×	×	Comparative steel	
40	35	0	0	0	×	×	×	Comparative steel	
	36	×	×	×	×	×	×	Comparative steel	
45	Note: Each corrosion resistance was evaluated on the basis of the steel of No. 36.								

## (continued)

# Claims

1. A corrosion-resistant steel product for crude oil tanker, comprising:

C: 0.03 to 0.16 mass%, Si: 0.05 to 1.50 mass%, Mn: 0.1 to 2.0 mass%, P: 0.025 mass% or lower, S: 0.01 mass% or lower, AI: 0.005 to 0.10 mass%, N: 0.008 mass% or lower, Cr: more than 0.1 mass% and 0.5 mass% or, lower and Cu: 0.03 to 0.5 mass% and, as an alternative addition element, one or two or more elements selected from W: 0.01 to 0.5 mass%, Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, Sb: 0.001 to 0.5 mass%, Ni: 0.005 to 0.3 mass%, and Co: 0.005 to 0.3 mass%, so that the components satisfy that the X value defined by Equation (1) is 0.5 or lower and the Y value defined by Equation (2) is 0.5 or lower;

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	X value = $(1 - 0.8 \times Cu^{0.5}) \times \{1 - (0.8 \times W + 0.4 \times$
5	Mo) <sup>0.3</sup> } × {1 - (0.8 × Sn + 0.8 × Sb) <sup>0.5</sup> } × {1 - (0.05 × Cr +
	$0.03 \times \text{Ni} + 0.03 \times \text{Co}^{0.3} \times (1 + \text{S/0.01} + \text{P/0.05})$ (1)
10	and
	Y value = $(1 - 0.3 \times Cr^{0.3}) \times \{1 - (0.8 \times W + 0.5 \times$
15	Mo) <sup>0.3</sup> } × {1 - (Sn + 0.4 × Sb) <sup>0.3</sup> } × {1 - (0.1 × Ni + 0.1 × Co
15	+ $0.05 \times Cu$ ) <sup>0.3</sup> } × {1 + (S/0.01 + P/0.08) <sup>0.3</sup> } (2);
20	and the balance containing Fe and inevitable impurities, and

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the balance containing Fe and inevitable impurities, and the element symbol of each equation representing the content (mass%) of each element.

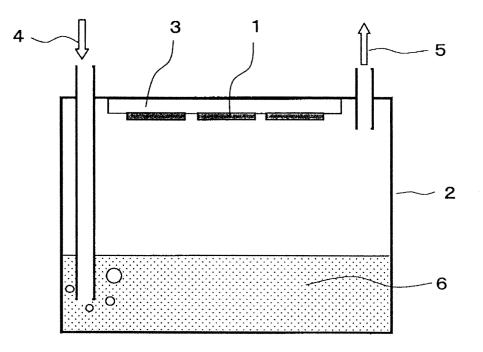
- 2. The corrosion-resistant steel product for crude oil tanker according to claim 1, comprising one or two or more elements selected from W: 0.01 to 0.5 mass%, Mo: 0.01 to 0.5 mass%, Sn: 0.001 to 0.2 mass%, and Sb: 0.001 to 0.5 mass% as the alternative addition element.
- 3. The corrosion-resistant steel product for crude oil tanker according to claim 2, further comprising one or two elements selected from Ni: 0.005 to 0.3 mass% and Co: 0.005 to 0.3 mass% in addition to the alternative addition elements.
- 30 4. The corrosion-resistant steel product for crude oil tanker according to any one of claims 1 to 3, further comprising one or two or more elements selected from Nb: 0.001 to 0.1 mass%, Ti: 0.001 to 0.1 mass%, Zr: 0.001 to 0.1 mass%, and V: 0.002 to 0.2 mass% in addition to the component composition.
  - 5. The corrosion-resistant steel product for crude oil tanker according to any one of claims 1 to 4, further comprising one or two or more elements selected from Ca: 0.0002 to 0.01 mass%, REM: 0.0002 to 0.015 mass%, and Y: 0.0001 to 0.1 mass% in addition to the component composition.
    - 6. The corrosion-resistant steel product for crude oil tanker according to any one of claims 1 to 5, further comprising B: 0.0002 to 0.003 mass% in addition to the component composition.
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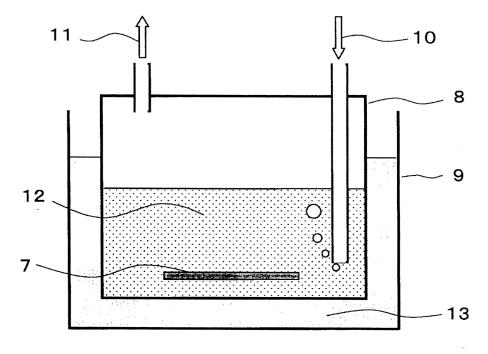
- 7. The corrosion-resistant steel product for crude oil tanker according to any one of claims 1 to 6, which is obtained by forming a primer coating film containing Zn on the surface of the steel product.
- The corrosion-resistant steel product for crude oil tanker according to any one of claims 1 to 7, which is obtained 8. 45 by forming an epoxy type coating film on the surface of the steel product.

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FIG. 1







	INTERNATIONAL SEARCH REPORT		International appli	
			PCT/JP2	009/071841
	CATION OF SUBJECT MATTER (2006.01)i, <i>C22C38/60</i> (2006.01)i	i		
According to Int	ernational Patent Classification (IPC) or to both nationa	l classification and IP	C	
B. FIELDS SE				
Minimum docur C22C38/00	nentation searched (classification system followed by cla -38/60	assification symbols)		
Jitsuyo		nt that such document tsuyo Shinan T proku Jitsuyo S	loroku Koho	1996-2010
	base consulted during the international search (name of c	data base and, where r	practicable, search te	rms used)
Category*	NTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where ap	propriate, of the relev	ant passages	Relevant to claim No.
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А	JP 2007-277616 A (Kobe Steel 25 October 2007 (25.10.2007), claims; paragraph [0043]; tab & CN 101050507 A		2, 4	1-8
A	WO 2007/116593 A1 (JFE Steel 18 October 2007 (18.10.2007), claims; table 1 & EP 2009125 A1 & CN & JP 2007-291494 A			1-8
× Further de	cuments are listed in the continuation of Box C.	See patent far	mily annex.	
<ul> <li>"A" document of to be of par</li> <li>"E" earlier applifiling date</li> <li>"L" document v cited to est special reas</li> <li>"O" document r</li> <li>"P" document p</li> </ul>	gories of cited documents: lefining the general state of the art which is not considered ticular relevance eation or patent but published on or after the international which may throw doubts on priority claim(s) or which is ablish the publication date of another citation or other on (as specified) eferring to an oral disclosure, use, exhibition or other means ublished prior to the international filing date but later than date claimed	<ul> <li>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</li> <li>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is taken alone</li> <li>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such document, such combination being obvious to a person skilled in the art</li> <li>"&amp;" document member of the same patent family</li> </ul>		
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<u> </u>	DOCUMENTS CONSIDERED TO BE RELEVANT		
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