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3,704,181

COLD ROLLED STEEL SHEET HAVING STABILIZED THIN OXIDE FILM AND
HAVING EXCELLENT RESISTANCE AGAINST CORROSION PARTICULARLY
INITIAL RUST FORMATION AS WELL AS AGAINST
CORROSION AFTER LACQUERING

Filed May 19, 1970

3 Sheets-Sheet 1

FIG. 1

Immersion Potential Curve

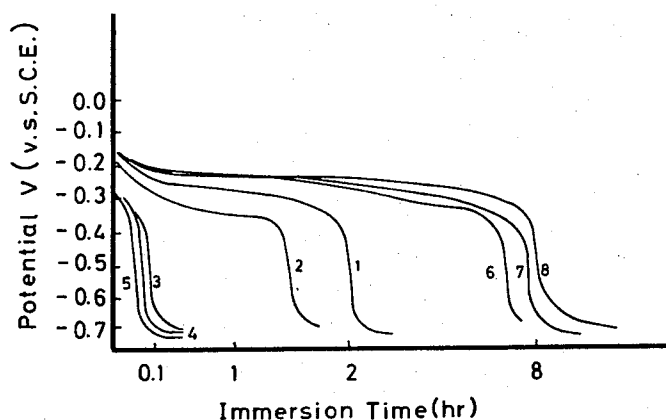
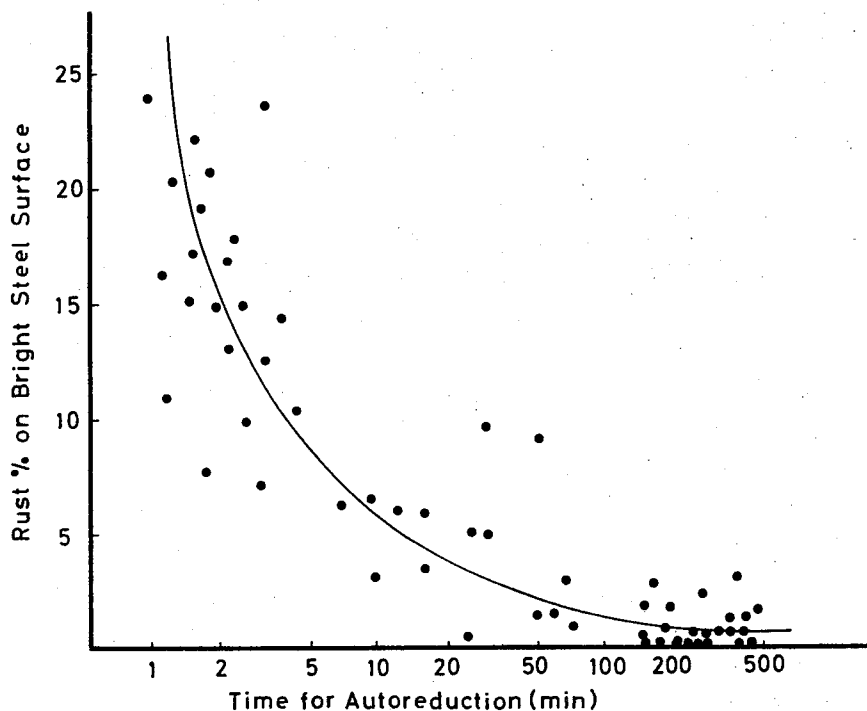


FIG. 2

Relation between Rust Percentage and
Time for Autoreduction of Oxide Film



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3 Sheets-Sheet 2

FIG. 3

Relation between Sb, Bi Content and
Time for Autoreduction

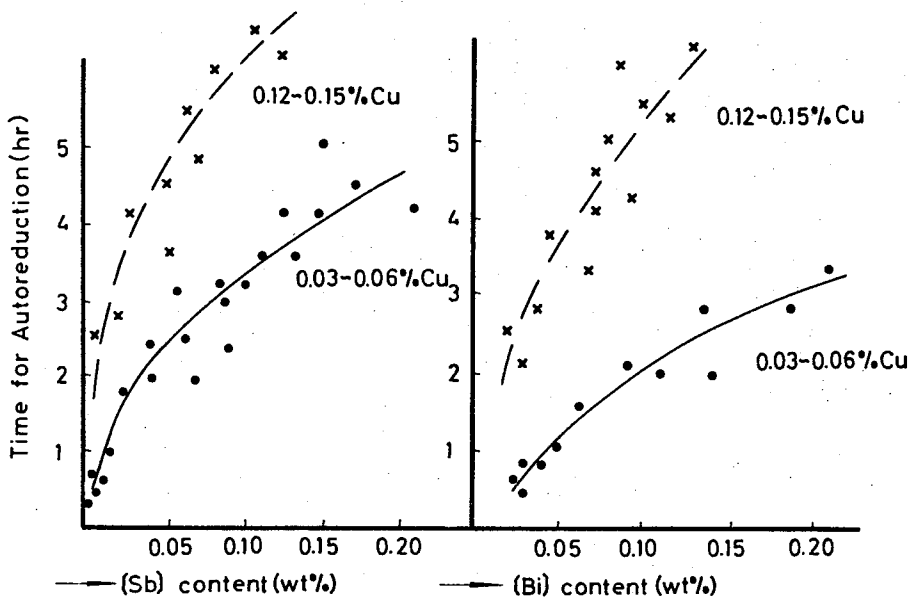
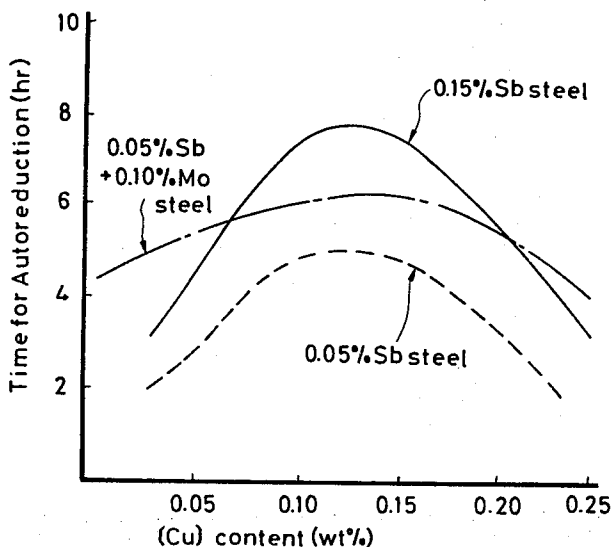


FIG. 4

Relation between Cu Content and
Time for Autoreduction



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3 Sheets-Sheet 3

FIG. 5

Relation between C, Mn, Si Content and
Time for Autoreduction

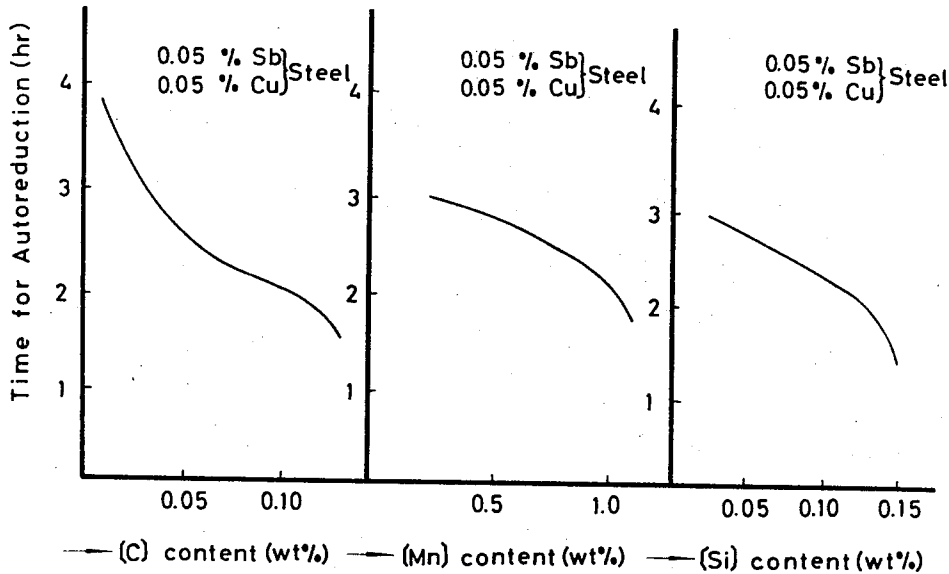
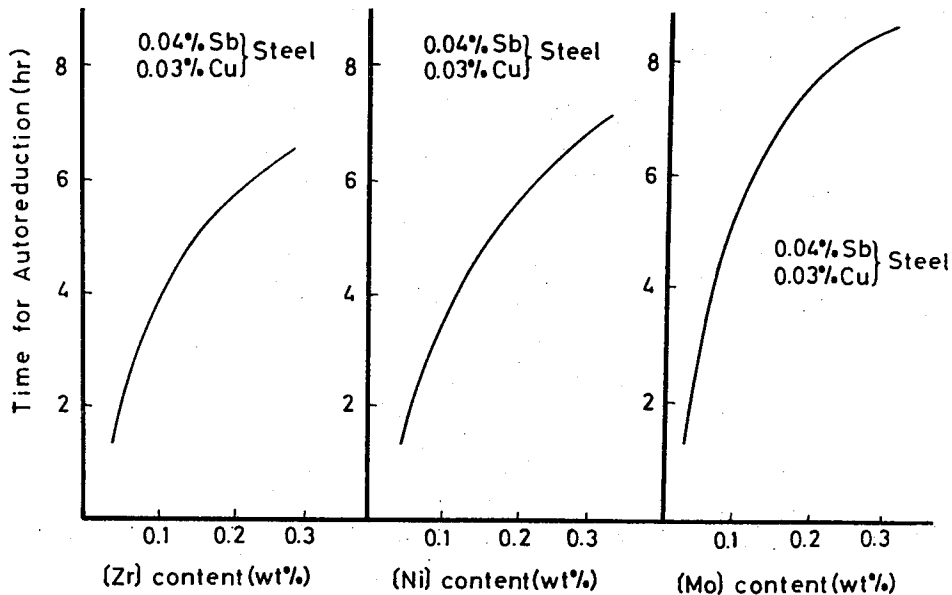


FIG. 6

Relation between Zr, Ni, Mo Content and
Time for Autoreduction



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COLD ROLLED STEEL SHEET HAVING STABILIZED THIN OXIDE FILM AND HAVING EXCELLENT RESISTANCE AGAINST CORROSION PARTICULARLY INITIAL RUST FORMATION AS WELL AS AGAINST CORROSION AFTER LACQUERING

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3 Claims

ABSTRACT OF THE DISCLOSURE

A cold rolled steel sheet containing as a basic components C≤0.12%, Mn 0.10–1.00%, Si≤0.15%, Cu 0.01–0.20%, Sb 0.01–0.20% and containing in case of necessity a small amount of Zr, Mo, and Ni, which steel sheet has excellent resistance against corrosion, particularly initial rust formation as well as corrosion after lacquering and provides high corrosion resistant material suitable for cans when the ratio of S to P is more than 1.

BACKGROUND OF THE INVENTION

The present invention relates to a cold rolled steel sheet having excellent resistance against corrosion, particularly against initial rust formation as well as against corrosion after lacquering.

The "initial rust" used herein means any rust formation of iron hydroxide (which transforms thereafter) observable by naked eye or a microscope, which takes place after the formation of a thin oxide film less than 100 Å on the fresh surface of iron and low alloy steels exposed to the atmospheric air.

Normally, when a steel sheet is, after rolling, subjected to mechanical workings such as drawing, expanding, cutting and grinding, a completely fresh metal surface appears, which is exposed to the atmospheric air. This exposed fresh surface is covered almost instantaneously by a thin oxide film (consisting essentially of γ -Fe₂O₃) less than 100 Å in the air.

This oxide film is not visible by the present measuring technics, and the fresh metal surface still retains completely metallic luster to the naked eye.

However, when the surface is exposed for a long period thereafter, rust formation takes place all over the whole surface in a short time in case of an ordinary low-alloy steel.

This rust formation first takes place at defects of the oxide film as mentioned above, and at its initial stage an iron oxide of high hydration is formed which progressively transforms into a higher oxide as the time passes. The formation of iron oxide is called as the initial rust formation and is visible by naked eyes or a microscope, which iron oxide extinguishes the metallic lustre as it progressively increases.

When an ordinary low-alloy steel is used after metal plating or organic coating, for example, as can production material, the steel material is usually blanked (or stamped) or cut into required shapes. The fresh surface exposed during the workings, for example, cross sections made by the cutting operation, has a very poor resistance against rust formation and in a short time the rust formation takes place which causes various difficulties in practical applications.

In order to overcome these difficulties, it may be con-

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sidered to apply an effective organic rust preventive coating to the surface, but this is not a satisfactory rust preventive method for protecting destructed portions of the coating caused during transportations after can production or during canning process. Therefore, importance of the resistance of the steel sheet by itself against the initial rust formation as a basic improvement is increasingly recognized.

The above fact is an important fact not only in the steel sheet for can production, but also in many applications in which thin gage steel sheets such as ones for automobile and electric appliances are used, particularly in applications in which commercial value of products is severely damaged.

The present inventors conducted various extensive researches and studies for developing steel sheet having excellent resistance against the initial rust formation, and have found that the nature and condition of the very thin oxide film less than 100 Å formed on the exposed fresh surfaces of iron and low alloy steels plays an important role in preventing the initial rust formation. Namely, when a steel sheet is left in the air, an amount of moisture corresponding to the humidity in the atmospheric air will deposit on the surface of the steel sheet, and in case of a defective oxide film a heavy rust formation is caused, while in case of a complete oxide film no rust formation is caused and the deposited moisture will wholly evaporate, causing no damage on the surface of the steel sheet.

Generally speaking, when a low-alloy steel is left in the atmosphere, the surface is more or less susceptible to red rust formation in a long run.

In the past, various methods were considered and proposed to preventing corrosion of steel by improving the steel itself, and may be classified into the following two groups. Namely, as seen in stainless steel, for example, one group of methods is to convert the steel itself into a noble metal by alloying it with corrosion resistant metals. In this case the metallic lustre is retained, but production cost is very high and thus the product is limitedly used only in special applications. The other group of methods is to prevent further progress of rust formation by the formation of dense oxide layer in a visible rust layer formed on the steel surface as seen in a series of low-alloy steels commonly called as atmosphere corrosion resistant steels. In this case the surface appearance is not regarded as important.

The cold rolled steel sheet having an excellent resistance to the initial rust formation aimed to by the present inventors has naturally different required properties from those required to stainless steels and atmosphere corrosion resistant steels.

Ordinary cold rolled steel sheets are usually subjected to a phosphate treatment and other substrate treatment for lacquering and then to lacquer coating before they are used in various applications such as automobile sheets and electrical appliances. However, for the substrate treatment for lacquering, very severe surface conditions must be met, and corrosion resistance after the lacquering is regarded as an important factor.

For improving the corrosion resistance after lacquering, all of the conventional arts are to improve the substrate treatment for enhancing properties of the substrate, and no try has been made to improve the corrosion resistance of the steel itself for enhancing the properties of lacquer coated steel sheet.

SUMMARY OF THE INVENTION

Therefore, a main object of the present invention is to provide a cold rolled steel sheet in which the thin oxide film formed on its surface can be rendered to be very dense and stabilized.

Another object of the present invention is to provide a cold rolled steel sheet having also good corrosion resistance after lacquering, in which a dense and stabilized thin oxide film is formable on fresh surfaces of the steel.

Still other object of the present invention is to provide a cold rolled thin gauge steel sheet suitable for cans, particularly cans for carbonated beverages, in which a dense and stabilized thin oxide film is formable on fresh surfaces of the steel.

Other objects of the present invention will be understood from the following descriptions and the attached drawings.

One of the main features of the present invention is that 0.01-0.20% by weight of copper and 0.01-0.20% by weight of antimony are added to a steel containing C<0.12%, Mn 0.1-1.00%, Si ≤0.15% with the balance being essentially iron. Without departure from the scope of the present invention at least one selected the group consisting of zirconium, molybdenum and nickel may be further added in an amount between 0.01-0.30%.

Another feature of the present invention is that the sulphur content is limited to 0.015-0.10% and the ratio of sulphur content to phosphorus content is limited to more than 1 (S/P>1) in case of a steel sheet suitable for can production. The whole or part of the antimony content may be replaced with bismuth. In this case 0.01-0.20% of bismuth in single or 0.01-0.20% of antimony plus bismuth may be contained.

The present steel sheets can be produced through smelting in an ordinary steel making furnace such as a converter and ordinary hot and cold rolling and annealing. As for the annealing, a box annealing is desirable.

The steel sheet having excellent resistance against the initial rust formation according to the present invention

FIG. 6 is a graph showing the relation between the contents of zirconium, nickel and molybdenum in the steel sheet and the time for autoreduction of oxide films.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As mentioned before, the present inventors have found that the oxide film formed naturally on the fresh exposed surface of iron or low alloy steels plays an important role for preventing the initial rust formation, and the present inventors have made extensive studies on effects of steel compositions on the characteristics of the oxide film.

The natural oxide film formed on the fresh exposed surface in the atmosphere grows to a thickness of about 20-40 Å. at most, and clarification of the structure and nature of the oxide film is not easy. However, the present inventors have succeeded in clarifying the co-relation between the oxide film and the resistance against the initial rust formation using electron diffraction technics and electro-chemical measuring technics.

Regarding an ordinary rust formation in which the rust is formed by the progress of atmospheric corrosion, it is an established theory accepted by experts that the rust formation is due to corrosion reactions in neutral solution. Based on this, the present inventors have investigated the characteristics of the oxide film using neutral solutions (sodium borate-chloric acid buffer solution of pH 7.65).

FIG. 1 shows the change by time in the natural electrode potential which appears when various steel sheets shown in Table I having natural oxide films formed in the atmosphere are immersed in the above neutral solutions.

TABLE I

(Chemical compositions of specimens by weight percent)

	C	Mn	P	S
Base steel sheets.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043
1. Sb contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.05% Sb
2. Bi contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.05% Bi
3. Cu contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.10% Cu
4. Mo contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.05% Mo
5. Base steel sheet.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043
6. Sb and Mo contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.1% Sb+0.05% Mo
7. Bi and Cu contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.1% Bi+0.13% Cu
8. Sb and Cu contained.....	<0.01	0.25-0.53	0.006-0.043	0.006-0.043 0.1% Sb+0.14% Cu

is useful as steel sheets for can production, automobile steel sheet, and steel sheets for electric appliances. When an ordinary low alloy steel is used in the above applications, the steel sheet is usually applied with metal coatings such as Sn, Cr, Zn and Al or subjected to a phosphate treatment or a chromic acid treatment (in some case an organic coating is further applied).

The present inventive steel sheet may be treated similarly, but the advantage of the present inventive steel sheet is that it is not susceptible to rust formation for a considerable period without any treatment, thus facilitating its transportation from steel makers to consumers and its storage.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing changes in immersion potentials of steel sheets of various compositions.

FIG. 2 is a graph showing the relation between the rust percentage and the time for autoreduction of oxide films.

FIG. 3 is a graph showing the relation between the contents of antimony and bismuth in the steel sheet and the time for autoreduction of oxide films.

FIG. 4 is a graph showing the relation between the copper content in the steel sheet and the time for autoreduction of oxide films.

FIG. 5 is a graph showing the relation between the contents of carbon, manganese and silicon in the steel sheet and the time for autoreduction of oxide films,

The general tendency is that a relatively noble potential of -0.2 v.--0.3 v. (U.S.S.C.E.) is observed at the initial stage of immersion and thereafter the potential lowers gradually and shows a sudden lowering after the lapse of certain period to about -0.7 v. which is near to the potential of a naked steel surface, where it again becomes constant. The initial high potential apparently corresponds to a potential observable under a condition in which an oxide film is present on the steel sheet surface, and the sudden lowering after the lapse of a certain period corresponds to the destruction (autoreduction dissolution) of the oxide film on the steel sheet surface. It is concluded from the above the oxide film is of more stable and less defect structure when the period for which the noble potential of about -0.3 v. is retained (the autoreduction time) is longer, and thus the resistance against the initial rust formation can be remarkably enhanced.

In FIG. 2 are shown the relation between the autoreduction time and the initial rust formation percentage observable by naked eyes. It is clear from FIG. 2 that the longer the autoreduction time is (the more stable the oxide film is), the lower the initial rust formation percentage is, thus proving the above conclusion. In FIG. 2, for the rusting test, the test specimens were stacked in a humidity cabinet which was controlled at 40° C., 90% relative humidity.

Next, the present inventors have further investigated the mechanism of prevention of the initial rust forma-

tion by the steel compositions, and have found that the alloying elements set forth in Table I in single or in combination remarkably stabilize the non-visible oxide film (mainly of γ -Fe₂O₃ as observed by the electron diffraction technics) formed on the steel surface.

Of the above basic composition, antimony (bismuth also similar effect) is found to have the highest effect of enhancing the resistance against the initial rust formation, and steels containing these alloying elements show more noble initial immersion potentials and longer time of oxide film destruction as compared with the steel (5 in Table I) containing none of these elements. From this it is clear that the addition of antimony reduces the defects of oxide film and increases remarkably resistance against the reduction dissolution of the film. (1 and 6 in FIG. 1). These tendencies are recognized also in the addition of bismuth (2 and 7 in FIG. 1).

The reason for limiting the contents of antimony and bismuth to a range of 0.01–0.20% is as seen in FIG. 3 that any substantial effect is not obtained with a content less than 0.01%, and the good effect of antimony and/or bismuth addition will saturate and the qualities of the steel sheet will be deteriorated with a content more than 0.20%. From the points of addition effects and economy, the preferable range of antimony and/or bismuth contents is 0.05–0.10%.

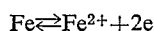
Copper content is an important factor in the present inventive steel sheet. Copper is an unavoidable element introduced in the steel during ordinary pig iron producing and steel making processes, and even by selective use of high-quality iron ore and advanced technics of converter steel making and so on, copper comes unavoidably into steel in a very small amount. As shown in FIG. 4, the present inventors have found that copper shows favourable effects only when it is used in combination with antimony and copper in single does not show any substantial effect. The effective range of copper content is 0.01–0.20% and the most desirable range is 0.08–0.18%. Beyond the above effective range, intermetallic compounds or α phase of copper precipitate, thus causing undesirable effects.

As a result of our basic experiments for clarifying the mechanism of resistance against the initial rust formation due to the steel compositions, it has been concluded that the effects of antimony and copper are based on the following mechanism.

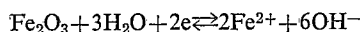
During the natural formation of iron oxide film, the antimony in solid solution in the steel is also oxidized, and a part of it comes into the oxide film and contributes to constitute the film in the form of Sb⁵⁺ but not in the form of Sb³⁺. However, it is not known whether the antimony gets into the lattice of iron oxide by replacement with Fe³⁺ ion or is localized as a simple oxide of Sb₂O₃ in particular portions of the iron oxide, for example in the defect portions of the oxide film.

Sb⁵⁺ ion has an oxidizing action and inhibits the reduction dissolution of the film. Namely, destruction (in a neutral solution and corresponds to atmospheric corrosion) of the film is generally takes the following auto-reduction reaction:

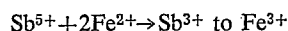
Anodic reaction:



Cathodic reaction:



But under the presence of Sb⁵⁺ ion the reaction is:



thus oxidizing Fe²⁺ to Fe³⁺.

Namely in the reduction of the film which is a cathodic reaction (the reaction of Fe³⁺→Fe²⁺ takes place in the lattices of iron oxide and then Fe²⁺ reacts with H₂O to

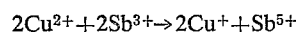
produce iron hydroxide and destroys the film), even when Fe²⁺ is formed in the lattice, Sb⁵⁺ present near it oxidizes instantly it into Fe³⁺, thus converting the oxide into its original state.

On the other hand, in the dissolution of iron which is an anodic reaction, Fe₂O₃ is formed by the oxidizing action of Sb⁵⁺ and fills up the defect portions of the film.

Copper which exhibits remarkable effect, particularly when added under the presence of antimony, is present in the steel in the state of solid solution, but is considered to be present in the oxide film in the form of Cu⁺ and Cu²⁺ ions. (the proportions of Cu⁺ and Cu²⁺ is not known).

Meanwhile, Sb takes the form of Sb³⁺ and Sb⁵⁺ (mainly Sb⁵⁺) in the oxide film, but the effect of enhancing the resistance against the initial rust formation is attributed to Sb⁵⁺ ion, as mentioned before.

However, Sb⁵⁺ itself is reduced to Sb³⁺ through its oxidation of Fe²⁺ ion into Fe³⁺ ion, and is oxidized by Cu²⁺ ion also present in the oxide film according to the reaction:



By the above reaction the resistance against the initial rust formation is enhanced.

Considering also from the ion radius, ions of higher atomic valence like Sb⁵⁺ or Cu²⁺ are easier to exist in the iron oxide, and Sb⁵⁺ is more stable than Cu²⁺ in the oxide, and thus the presence of Cu²⁺ ion gives a large effect on the resistance against the initial rust formation.

When copper is present in an amount more than intermetallic compounds or copper phase is caused to precipitate, which causes the formation of local cells which in turn cause corrosion, thus lowering the resistance against the initial rust formation.

It is already known that antimony content or antimony-copper content in steels is effective for acid resistance, particularly resistance against sulfuric acid. However an oxide film on the steel surface is easily dissolved and removed off in an acidic solution, and thus the corrosion reaction in such a medium proceeds in an electro-chemical reaction in which iron dissolves (Fe=Fe²⁺+2e) in the anodic reaction and hydrogen generates (2H⁺+2e=H₂) in the cathodic reaction. In this case, therefore, it is enough to suppress either one or both of the iron dissolution and the hydrogen generation in order to inhibit the corrosion. The effect of Sb—Cu on the acid resistance derives from its suppressing effects on the both reactions, which are considered to be due to the presence of the Sb—Cu intermetallic compounds.

The rust prevention in the present invention that the rust formation is prevented by stabilizing the oxide film itself through the above mentioned mechanism in corrosive media where corrosion proceeds under the presence of an oxide film is completely different from that of acid resistant steels in its object and mechanism.

Further, in the present invention the remarkable resistance against the initial rust formation is assured by addition of molybdenum nickel and zirconium, and if the steel sheet is used for production of cans for carbonated beverages the relation of S/P>1 is retained so that the sulphur content in the steel sheet is effective for suppressing corrosion by the carbonated substances and at the same time the initial rust formation and the surface rust of the steel sheet are prevented by the action of Sb—Cu content. Therefore, the technical thought of the present invention is clearly different from that of conventional acid resistant steels. Meanwhile the addition of copper in single exhibits no substantial effect as clearly shown in FIG. 1 (see 3).

As above described, the steel sheet according to the present invention has a very stable and dense oxide film formed thereon, and the oxide film is stable and no Fe ion dissolves into a paint film even when lacquering and an anodic treatment such as an electrodeposition of paint, for example, are given to the steel surface, and thus a

very excellent corrosion resistance even after lacquering and painting is obtained.

The reasons for limitations of elements other than antimony (bismuth) and copper in the present invention will be set forth hereinafter.

Carbon is useful only for obtaining the required mechanical strength, but tends to deteriorate the resistance against the initial rust formation. Namely, as clearly shown in FIG. 5, carbon shortens the autoreduction time and damages the stability of oxide film, and thus carbon should be not more than 0.12%, preferably not more than 0.10%. Lowering of the carbon content may be done by a vacuum degassing treatment during the steel making process or by a decarburization annealing during hot and cold rolling processes.

Manganese is added chiefly for preventing hot embrittlement due to sulphur, and is controlled between 0.10–1.00% depending on the sulphur content.

For the resistance against the initial rust formation, a lower manganese content is desirable (see FIG. 5).

Silicon should be as low as possible because it gives adverse effects on both the mechanical properties and the resistance against initial rust formation, and the silicon content is limited to not more than 0.15% in the present invention.

Phosphorus and sulphur is limited so as to meet the condition of $S/P > 1$ in which S is 0.015–0.100% in case a special control is required by applications, particularly in case the steel contacts with substances which contain or generate carbonic acid gas and corrosion is caused by phosphoric acid, namely in case the steel is used as material for production of cans for carbonated beverages, such as Coca-Cola.

Sulphur which is present in the steel in the form of MnS corrodes into corrosive media and acts as inhibitor for the steel sheet. Although control on the contents of sulphur and phosphorus does not exert substantial influence on the resistance against the initial rust formation, it is desirable to maintain the sulphur content between 0.015–0.03%.

As described above, when considering the present inventive steel sheet as material for can production, resistance against corrosion by can contents is assured by the sulphur content, and the resistance against rust formation at the outer side of the can is assured mainly by antimony and copper, and thus an excellent corrosion resistance as can material is assured by the combined effects.

Zirconium, nickel and molybdenum produce only a little effect if they are added in single, but their effects are remarkably enhanced if contained under the presence of antimony. Their contents less than 0.01% are not effective while their contents more than 0.3% cause material embrittlement and their effects tend to saturate, thus causing a considerable economical waste, as seen in FIG. 6. Therefore, their contents are limited to 0.01–0.30% for each element in the present invention, and their preferable ranges are 0.06–0.10% for zirconium, 0.08–0.15% for nickel and 0.03–0.08% for molybdenum. Combined addition of zirconium nickel and molybdenum also exerts similar effects and the total amount of zirconium nickel and molybdenum less than 0.6% is enough.

The fact that when the present inventive steel sheet is used as substrate for metal plating or conversion treatments such as a phosphate treatment, remarkably improved corrosion resistance at the plated surface in the atmospheric air is obtained is well understood from the fact that the resistance against rust formation on the steel surface at pinholes of the plating layer is high.

The present invention will be well understood from the following embodiments.

Example 1

The steel compositions set forth in Table 2 are obtained by reducing the carbon content of the steel of

basic composition prepared in a converter to less than 0.01% with a vacuum degassing and adding required alloying elements. Their corrosion resistance is shown by way of their rust resistance and their corrosion resistance after lacquering.

The relation between the corrosion resistance and elements other than carbon is explained under.

Specimen 1 is an ordinary steel, and Specimen 2 is a weather resistant steel containing increased amounts of copper and phosphorous. Their resistance against the initial rust formation is poor and their corrosion resistance after lacquering is bad. Specimens 3, 4 and 5, in which rust resistance and corrosion resistance after lacquering are improved to some extent by the addition of antimony or antimony and molybdenum, exhibit only unsatisfactory corrosion resistance due to the excessive content of copper.

Specimens 6 and 7 which are the steels according to the present invention exhibit very excellent rust resistance and corrosion resistance after lacquering due to the copper content which is limited to 0.08–0.10% and the addition of antimony, molybdenum nickel and zirconium.

Example 2

Table 3 shows corrosion resistance of the present inventive steels (Specimens Nos. 3, 4, 5, 7, 8, 9 and 10). Specimens Nos. 1 to 5 are prepared by adding alloying elements such as antimony, molybdenum, nickel, and zirconium to steel melt in a converter, with a carbon content level as seen in soft steel. Specimens Nos. 6–10 are prepared by lowering carbon content with a vacuum degassing treatment and adding alloying elements such as antimony, molybdenum, nickel and zirconium, and all of the specimens are Al-killed steel. Specimen No. 1 is a comparative steel in which the alloying element is not added. By Specimens Nos. 2 and 6 the effect by the addition of antimony alone is shown, and by Specimens Nos. 3, 4, 5, 7, 8, 9 and 10, the corrosion resistance obtained by the combined addition of antimony, molybdenum, nickel and zirconium is shown.

From Table 3 it is clear that steels containing a lower carbon content show better corrosion resistance, and steels containing copper and antimony and steels containing one or more of molybdenum, nickel, zirconium in addition to copper and antimony show excellent corrosion resistance.

Example 3

Table 4 shows steel compositions and their corrosion resistance when used as steel sheet for carbonated beverage cans.

Evaluation of the corrosion resistance is made as under.

(1) Corrosion resistance of can inside.—Specimens were immersed in a commercially available phosphate carbonated beverage at 27° C. for 4 days and corrosion rate was determined by measurement of weight loss.

(2) Corrosion resistance of can inside.—Specimens were stacked in a humidity cabinet (30° C., 85% relative humidity) for one month and red rust formation (percent) on the specimen surfaces were observed.

(3) General evaluation.—Corrosion resistance on can inside and outside of specimens was classified into several ranks and general evaluation was made on the base of the can inside corrosion and the can outside corrosion. Smaller values indicate better corrosion resistance as material for can production.

In Table 4, Specimens No. 1 and Nos. 11–15 are the present inventive steel, which were produced according to conventional production processes for cold rolled steel sheet including steel making in a converter, cogging, rolling and so on.

Of the specimens set forth in Table 4, Specimen No. 2 contain no antimony and shows poor corrosion resistance on can outside, and Specimen No. 4 shows still poor corrosion resistance on can outside due to the increased con-

tent of copper. Although Specimen No. 3 shows slightly improved corrosion resistance on can outside by the addition of antimony as compared with Specimen No. 4, its general evaluation is still unsatisfactory due to the high content of copper.

In Specimens Nos. 5-8, the ratio of S/P is less than 1 and the corrosion resistance on can outside is a medium grade, but the corrosion resistance on can inside is poor, thus these specimens are not satisfactory as material for can production.

In Specimens Nos. 9 and 10 the ratio of S/P is more than 1, but no antimony is added and the corrosion resistance on can outside is poor. Thus these specimens are not satisfactory.

Specimens No. 1 and Nos. 11-15 are prepared from the present inventive steel, which contain antimony and maintain the copper content in a lower side, with the ratio of S/P being more than 1, exhibit excellent corrosion resistance both on can inside and can outside, thus very excellent material for can production.

The present invention should not be limited to the above examples and various modifications and alterations can be made without departing from the scope of the present invention.

Remarks:

Ranking			
Can inside		Can outside	
$\mu\text{A./cm.}^2$	Ranking	Percent	Ranking
Less than 10.....	1	Less than 1.....	1
Less than 20.....	2	Less than 2.....	2
Less than 30.....	3	Less than 3.....	3
		Less than 5.....	4
		5-10.....	5
		10-15.....	6
		15-20.....	7
		20-25.....	8
		25-30.....	9
		30-35.....	10

What is claimed is:

1. A cold rolled steel sheet for the manufacture of carbonated beverage cans, having a stable oxide film formed thereon and having excellent resistance against initial rust formation as well as against corrosion after lacquering, consisting essentially of $C \leq 0.12\%$, $0.1-1.00\%$ Mn,

TABLE 2.—STEEL COMPOSITIONS, RUST RESISTANCE AND CORROSION RESISTANCE AFTER LACQUERING

Specimen number	Chemical compositions, percent by weight										Rust resistance ¹ (month)	Corrosion resistance after lacquering ² (mm.)
	C	Si	Mn	P	S	Cu	Sb	Mo	Ni	Zr		
Comparative steel:												
1.....	0.006	0.02	0.29	0.014	0.015	0.04	-----	-----	-----	-----	1.5	30
2.....	0.007	0.01	0.36	0.031	0.012	0.36	-----	-----	-----	-----	1.0	30
3.....	0.006	0.01	0.21	0.011	0.011	0.25	0.084	-----	-----	-----	2.5	15
4.....	0.006	0.02	0.18	0.013	0.009	0.30	0.151	-----	-----	-----	3.0	10
5.....	0.005	0.01	0.27	0.011	0.015	0.32	0.081	0.040	-----	-----	3.5	10
Inventive steel:												
6.....	0.007	0.02	0.24	0.014	0.013	0.08	0.073	-----	-----	-----	10.0	9
7.....	0.006	0.01	0.31	0.009	0.014	0.10	0.080	0.051	-----	0.034	11.5	8

¹ Evaluation of the rust resistance was made by stacking specimens in a humidity box at 30° C., 85% humidity, and the period until red brownish rust is formed over the whole of a clean steel surface without rust was measured.

² The corrosion resistance after lacquering was determined by applying a phosphate treatment to a steel sheet, coating an amino-alkyd paint thereon, scratching the paint coating, subjecting the sheet to a salt spray test (30 days) and measuring the width of blistered coating layer at the scratched portions.

TABLE 3.—STEEL COMPOSITIONS, RUST RESISTANCE AND CORROSION RESISTANCE AFTER LACQUERING

Specimen number	Chemical compositions, percent by weight										Rust resistance (month)	Corrosion resistance after lacquering (mm.)
	C	Si	Mn	P	S	Cu	Sb	Mo	Ni	Zr		
Comparative steel 1.....	0.06	<0.01	0.36	0.017	0.011	0.04	-----	-----	-----	-----	1.0	30
Inventive steel:												
2.....	0.05	0.01	0.29	0.012	0.018	0.06	0.110	-----	-----	-----	9.0	15
3.....	0.05	<0.01	0.27	0.014	0.011	0.08	0.072	0.051	-----	-----	10.0	18
4.....	0.07	<0.01	0.31	0.015	0.012	0.09	0.065	-----	0.081	-----	11.0	15
5.....	0.06	<0.01	0.25	0.013	0.015	0.08	0.089	-----	-----	0.051	11.0	12
6.....	0.006	<0.01	0.28	0.008	0.010	0.10	0.132	-----	-----	-----	10.0	13
7.....	0.005	<0.01	0.26	0.011	0.013	0.09	0.081	0.045	-----	-----	10.0	15
8.....	0.008	<0.01	0.25	0.013	0.011	0.09	0.059	-----	0.130	-----	11.0	12
9.....	0.008	<0.01	0.27	0.011	0.014	0.10	0.076	0.038	0.025	-----	11.5	12
10.....	0.007	<0.01	0.26	0.008	0.009	0.09	0.071	0.053	0.038	0.041	12.5	10

TABLE 4.—STEEL COMPOSITIONS AND CORROSION RESISTANCE

Specimen number	Chemical compositions, percent by weight								Corrosion resistance				Evaluation of total ranking
									Can inside		Can outside		
	C	Si	Mn	P	S	Cu	Sb	Mo	A./cm. ²	Ranking	Percent	Ranking	
Inventive steel 1.....	<0.11	0.01	0.40	0.013	0.029	0.03	0.040	-----	16	(2)	4	(4)	6
Comparative steel:													
2.....	0.09	0.01	0.38	0.015	0.026	0.04	-----	-----	18	(2)	23	(8)	10
3.....	0.10	0.01	0.42	0.015	0.032	0.28	0.039	-----	14	(2)	21	(8)	10
4.....	0.09	0.01	0.39	0.014	0.022	0.33	-----	-----	20	(2)	35	(10)	12
5.....	0.08	0.01	0.37	0.030	0.016	0.04	0.043	-----	103	(11)	1	(2)	13
6.....	0.10	0.01	0.40	0.035	0.020	0.05	-----	-----	74	(7)	10	(5)	12
7.....	0.08	0.01	0.27	0.031	0.012	0.26	0.041	-----	97	(10)	13	(6)	16
8.....	0.11	0.01	0.30	0.023	0.014	0.30	-----	-----	85	(9)	25	(8)	17
9.....	0.07	0.01	0.31	0.016	0.025	0.03	-----	-----	19	(2)	25	(8)	10
10.....	0.08	0.01	0.29	0.008	0.021	0.04	-----	-----	11	(2)	27	(9)	11
Inventive steel:													
11.....	0.07	0.01	0.35	0.012	0.029	0.04	0.031	-----	13	(2)	5	(4)	6
12.....	0.10	0.01	0.38	0.015	0.026	0.05	0.058	-----	18	(2)	2	(3)	5
13.....	0.06	0.01	0.55	0.011	0.031	0.04	0.114	-----	9	(1)	0.5	(1)	2
14.....	0.08	0.01	0.60	0.012	0.033	0.04	0.031	-----	13	(2)	2	(3)	5
15.....	0.08	0.01	0.40	0.011	0.031	0.05	0.025	0.045	8	(1)	1	(2)	3

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Si $\leq$ 0.15%, 0.015–0.10% S, 0.01–0.20% Cu, 0.01–0.20% Sb, and S and P under the condition of S/P>1, with the balance being iron and unavoidable impurities.

2. A cold rolled steel sheet for the manufacture of carbonated beverage cans, having a stable oxide film formed thereon and having excellent resistance against initial rust formation as well as against corrosion after lacquering, consisting essentially of C $\leq$ 0.12%, 0.1–1.0% Mn, Si<0.15%, 0.015–0.10% S under the condition of S/P>1, 0.01–0.20% Cu, 0.01–0.20% Sb, and at least one selected from the group consisting of Zr, Mo, and Ni in an amount of 0.01–0.30%, with the balance being iron and unavoidable impurities.

3. A cold rolled steel sheet according to claim 1 in which the copper content is 0.08–0.15%.

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References Cited

UNITED STATES PATENTS

3,459,538	8/1969	Teramae et al.	75—125
3,303,060	2/1967	Shimizu et al.	148—2 X
3,239,388	3/1966	Sasaki	148—2
2,867,531	1/1959	Holzwarth et al.	75—123 A
2,053,846	9/1936	Schulz et al.	75—123 A
3,368,886	2/1968	Muta et al.	148—36 X

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