

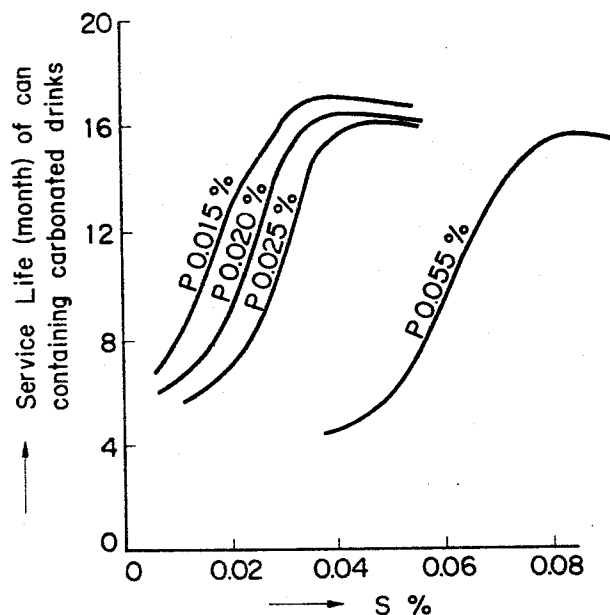
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STEEL PLATES FOR CANS USED FOR CANNING CARBONATED DRINKS

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STEEL PLATES FOR CANS USED FOR CANNING CARBONATED DRINKS

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This invention relates to a steel plate for cans used for canning substances containing or generating carbon dioxide, in particular, for canning carbonated drinks.

Steel cans have been widely used at present for refreshing drinks, fruit juices and the like and these steel cans are required to have the corrosion resistance of longer than 6 months. The steel cans which are marketed at present or have standardized chemical compositions are provided with sufficient corrosion resistance as cans for substances containing organic acids such as fruit juice, etc., but their corrosion resistances are insufficient for carbonated drinks. That is, in the case of using such a steel can for canning carbonated drinks, corroded holes are very easily formed at the can walls. This is because the corrosion mechanism by the carbonated drink is different from that by a drink containing an organic acid, such as, fruit juice.

In a steel can for a fruit juice mainly consisting of organic acids, the steel plate for the can having the above-mentioned known composition is generally tin-plated and hence the plated tin acts electrochemically as anode to the base metal when the can contains the juice. Therefore, even in the case where the base metal of the steel plate is exposed to the organic acid at the pin-holed portions of the plating surface, the exposed base metal can also be protected sufficiently by the tin electrochemically.

On the other hand, since the base iron of the tin-plated steel can acts as anode to the plated tin in a carbonated drink, the base iron exposed at the pin-holed portions cannot be protected by the plated tin and hence an accident easily occurs that the exposed base metal of the can is dissolved out to form perforations.

Further, since tin is generally easily dissolved by carbonated drinks and hence the base iron cannot be sufficiently protected from the attack by carbonated drinks by only tin plating, it has been proposed to coat the can with a lacquer and the like. However, even in such a case it is impossible to cover completely the surface of the can and consequently it is necessary to improve the corrosion resistance of the base steel.

An object of this invention is to provide a steel plate for can having a high corrosion resistance to carbonated drinks by adjusting the composition of the steel plate.

Another object of this invention is to provide at a low cost a steel plate for cans used for canning carbonated drinks.

Those and still other objects of this invention will become clear from the following descriptions of our invention.

The accompanying drawing is a graph showing the relation between the amounts of P and S contained in a steel plate and the corrosion resistance of the plate to a carbonated drink.

As mentioned above, the corrosion mechanism of steel plate by a fruit juice mainly consisting of organic acids is completely different from that by a carbonated drink but the inventors have found, as the results of various experiments, that in a steel plate (tin-plate) used for canning carbonated drinks, in particular, for a carbonated drink containing phosphoric acid as the base component, the proportions of elements contained in the steel, particularly,

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the ratio of sulfur to phosphorus, give an important influence on the improvement of the corrosion resistance.

That is, if the content of phosphorus in the steel plate for can is increased, the corrosion of the metal by the carbonated drink is increased and accordingly there is a tendency that perforations are easily formed by the corrosion.

However, it has been found that by giving sulfur in the steel, the formation of perforations in the can wall by the corrosion can be effectively prevented.

The addition of sulfur to steel to be subjected to cutting working has been conducted and there are known as S-containing free-cutting steel, for example, A.I.S.I. C 1108, C 1109, etc., but in such a known art, sulfur is added to improve the cutting property of steel and hence the known art is completely different from our invention in the purpose of the addition of sulfur and the field of using the S-containing steel.

In the graph of the accompanying drawing, which illustrates the relation of the amounts of S (percent) and P (percent) in a tin-plate can (C, 0.11–0.08%, Si, 0.01–0.015% and Mn, 0.4–0.5%) containing as a carbonated drink Coca Cola (registered trade name) and the service life (month) of can (indicated by a period, during which 10% of the tested cans become the perforated ones), it is clearly shown that the higher the content of S is against the content of P, the more the service life of can is improved, and even the service life of a tin-plate can containing a large proportion of P can be extended more than twice by adding S in an amount larger than the content of P. Nevertheless, it is not preferable to increase the content of phosphorus in steel but it is clear that the content of phosphorus is not necessarily reduced forcibly by a complicated and troublesome method.

In the fundamental feature of this invention, sulfur is incorporated in a steel can for a carbonated drink of a phosphoric acid base in such amount that the content of sulfur is larger than the content of phosphorus present in the steel. However, since the presence of a too large proportion of sulfur in steel causes the formation of a large amount of sulfides during the step of manufacturing the steel plate and hence makes the steel fragile, for example, causes cracking in the steel during hot rolling step, the content of sulfur must be less than 0.1%. Further, as mentioned above, the content of sulfur must be always larger than that of phosphorus and the lower limit of sulfur shall be determined considering the relation with the content of phosphorus, but if the content of sulfur is less than 0.02%, sufficient corrosion resistance to the carbonated drink cannot be obtained. That is, in the present invention it is necessary that the content of sulfur is equivalent to or higher than the content of phosphorus in the S-content range of 0.02 to 0.1%, preferably 0.025 to 0.040%.

Accordingly, in case of producing a steel plate containing a large proportion of phosphorus, sulfur must be positively added to the steel in the refining step thereof.

For the improvement of corrosion resistance of steel, the content of phosphorus is preferably small. However, it is impossible in the steel manufacturing techniques to remove phosphorus completely and usually steel contains about 0.015% of phosphorus inevitably. The corrosion resistance of such a steel can sufficiently be increased if the ratio of S/P in the steel is higher than 1 in accordance with this invention without forcibly reducing the content of phosphorus. However, by the reason mentioned above, the content of phosphorus may be less than 0.1% (not including 0.1%).

According to the present invention, the content of sulfur is defined to be 0.01 to 0.1%, which makes unnecessary the severe conditions about desulfurization, and sul-

fur is rather added positively as the case may be. Thus, by the present invention steel plates having desired corrosion resistance can be obtained very economically.

As mentioned above, sulfur is very effective as an element for suppressing the corrosion promoting action of phosphorus in a steel plate as a can for a carbonated drink containing phosphoric acid as the base. On the other hand the inventors have found, however, that in the case of canning a carbonated drink containing as the base citric acid and/or tartaric acid, copper is effective for suppressing the corrosion promoting action of phosphorus. The action of copper is similar to the above-mentioned action by sulfur, and in the case of adding copper in steel, the content must be higher than that of phosphorus and preferably be 0.1–0.3%. If the substance to be charged is a specific one, sulfur or copper may be added as the corrosion suppressing agent according to the kind of the carbonated drinks but if sulfur and copper are added at the same time, the steel cans can be used for canning both kinds of carbonated drinks. In the latter case, the content of sulfur is also of course adjusted to 0.02 to 0.1% such that the ratio of P/S is less than 1. Thus, by adjusting the ratio of P/S in steel to less than 1 and the content of Cu in the steel to 0.1 to 0.3, the steel plate having sufficient corrosion resistance to any kinds of carbonated drinks can be obtained.

The content of copper is defined to the above-mentioned range since if the content is less than 0.1% the sufficient corrosion resistance to the carbonated drink cannot be obtained, while if the content is higher than 0.3% the presence of copper causes cracking or surface roughening of the steel plate during hot working.

In the invention, besides above-mentioned phosphorus and sulfur and/or copper, may be present 0.02 to 0.20% of carbon, less than 0.3% of silicon and 0.02 to 1.0% of manganese.

The content of C is defined as above since the content of C in steel is less than 0.02%, the steel becomes too soft to provide a necessary strength and further if the content is higher than 0.2% cold rolling for the steel becomes difficult.

Si is added in the system during the production of steel for the purpose of refining but the content of Si shall be defined to be less than 0.3%. If the content of Si is higher than the value, the workability of the steel is reduced, which makes the steel unprofitable for can making materials.

Mn is added in order to prevent the steel from becoming hot fragile by the presence of sulfur as well as to obtain mechanical properties such as hardness and tensile strength necessary for the production of cans, but it is necessary that the content of Mn is from three times to ten times as large as that of S in a range of the Mn

ingot was, after blooming, subjected to hot rolling and cold rolling. The hot rolling conditions were as follows:

Finishing temperature, ° C. ----- 880
Coiling temperature, ° C. ----- 630
Plate thickness, mm. ----- 2.3

The thickness of the plate was reduced to 0.25 mm. by the cold rolling. Thereafter, the steel was subjected to continuous annealing and then to skin pass rolling at the reduction ratio of 1.0%. After cleaning the surface of thus obtained steel plate, the steel plate was plated with tin in the thickness of 0.9 micron and then coated with a lacquer, and made cans.

The results of charging in thus prepared can Coca-Cola as a carbonated drink are shown in Table 1.

TABLE 1.—CAN COMPOSITION (EXCEPT Fe) AND THE SERVICE LIFE OF CAN

	Chemical Component (percent)					Service Life (months)
	C	Mn	Si	P	S	
1.....	0.11	0.50	0.01	0.03	0.05	15
2.....	0.11	0.50	0.01	0.025	0.035	14
3.....	0.11	0.50	0.01	0.014	0.035	17
4.....	0.08	0.50	0.015	0.045	0.050	15
5.....	0.08	0.40	0.01	0.02	0.020	9

NOTE.—(1) The service life is defined by the period, in which 10% of the tested cans become perforated ones;
(2) The storage temperature is 38° C.

In Table 1, Sample No. 5 stands for a conventional steel plate. As shown in the table the life of the conventional steel plate is less than that of the can material of this invention shown in the table as sample numbers 1 to 4 while the former contains a lower amount of P and S than the latter, which shows that the steel can of this invention has a very excellent corrosion resistance.

EXAMPLE 2

Steel ingot containing various components was manufactured by melting each of the test material in a converter while reducing the content of P as low as possible and then adding a desired amount of S and Cu into the molten steel and, after blooming, was subjected to hot rolling and cold rolling to provide the steel plate of 0.25 mm. in thickness. The hot rolling conditions were same as in Example 1. After subjecting it to continuous annealing, the steel plate was subjected to skin pass rolling at a reduction ratio of 1%. After pickling and water-rinsing, the steel plate was plated with tin in the thickness of 0.4 micron and after coating with a lacquer, made can. The results of conducting corrosion tests about thus prepared steel can while charging therein the carbonated drinks shown in the table are shown in Table 2, in which a test results about a conventional steel can are shown for comparison.

TABLE 2.—CAN COMPOSITION (EXCEPT Fe) AND SERVICE LIFE OF CAN

	Chemical Component (percent by weight)						Service Life (months)		
	C	Mn	Si	P	S	Cu	(A)	(B)	(C)
1.....	0.10	0.50	0.01	0.017	0.035	0.25	16	19	20
2.....	0.10	0.50	0.01	0.030	0.020	0.30	8	18	20
3.....	0.10	0.50	0.01	0.017	0.027	0.25	13	18	21
4.....	0.10	0.50	0.01	0.014	0.035	0.20	17	19	21
5.....	0.10	0.50	0.01	0.017	0.017	0.06	9	13	15

NOTE.—(1) The service life of can is same as in Table 1; (2) Storage temperature is 38° C.

content being less than 1.0%. Accordingly, it is most preferable that the content of Mn in the steel plate for can of this invention is in a range of 0.3 to 0.5%.

EXAMPLE 1

The sample material having the composition shown in below Table 1 was melted in a converter and at making ingot, sulfur powders were added to adjust the proportion of sulfur. The steel ingot was 12 ton capped ingot. The

In Table 2, the sample shown by number 5 is a conventional steel can. The results showed that the can materials of this invention, that is, ones shown by numbers 1, 3 and 4 in the table had excellent corrosion resistance to the all carbonated drinks as compared with the conventional one. Further, the sample of number 2 had a lower corrosion resistance to the carbonated drink of a phosphoric acid base but had a good corrosion resistance to other carbonated drinks, which shows that the effect of Cu appears clearly.

EXAMPLE 3

The steel can having the composition shown in below Table 3 was prepared by the following steps. That is, a steel ingot was manufactured from a molten steel produced in an experimental vacuum melting furnace. The steel ingot was hot rolled at a finishing temperature of 810–910° C. into a steel plate of 2.3 mm. in thickness and after pickling was cold rolled into the plate of 0.25 mm. in thickness.

The cold rolled plate was annealed for 2 hours at 650° C. in a HNX gas atmosphere (CO₂ 0.05% by volume, CO 0.05%, H₂ 3–10%, and rest N₂). Thereafter, the plate was subjected to skin pass rolling with the reduction ratio of 1% and after pickling was tin-plated.

The corrosion test was conducted by immersing thus prepared steel plate in carbonated drinks of citric acid type and tartaric acid type. The results are shown in Table 3.

TABLE 3.—COMPOSITION (EXCEPT Fe) AND SERVICE LIFE

	Chemical Component (Percent by weight)					Service Life (months)		
	C	Mn	Si	P	S	Cu	(A)	(B)
1.....	0.075	0.49	0.082	0.028	0.01	0.23	16	16
2.....	0.08	0.71	0.025	0.041	0.016	0.22	14	14
3.....	0.06	0.68	0.028	0.015	0.008	0.26	16	17
4.....	0.077	0.74	0.030	0.043	0.024	0.046	8	9

NOTE.—(1) The service life is same as in Table 1; (2) The experimental temperature is 67° C.; (3) (A) stands for the carbonated drink of citric acid type and (B) stands for the carbonated drink of tartaric acid type.

As clear from the above results about the samples shown by numbers 1 to 3, it is shown that even when the content of P is higher than that of S, the corrosion resistance of the steel plate to the carbonated drink of a citric acid base or a tartaric acid base is improved by the addition of Cu in a proportion of higher than 0.1% and further higher than that of P. The sample of number 4 was a control sample and it is observed that since the contents of Cu, P and S were out of the range of this invention, the life of the steel plate was very short.

What is claimed is:

1. A steel plate as a can material for carbonated drinks comprising 0.02 to 0.20% by weight of carbon, 0.02 to 1.00% by weight of manganese, less than 0.3% by weight of silicon, and at least one member selected from the group consisting of 0.02 to 0.10% by weight of sulfur and 0.1 to 0.3% by weight of copper, balance being iron

and unavoidable impurities including phosphorus, the content of said phosphorus being always less than the contents of said sulfur and copper.

2. The steel plate according to claim 1 wherein said carbonated drink is a phosphoric acid type carbonated drink, said member is 0.02 to 0.10% by weight of sulfur, and the content of said sulfur is always higher than that of said phosphorus.

3. The steel plate according to claim 1 wherein said carbonated drink is a citric acid type carbonated drink, said member is sulfur and copper, and the content of said copper is always higher than that of said phosphorus even in the case where the content of phosphorus is higher than that of sulfur.

4. The steel plate according to claim 1 wherein said carbonated drink is a tartaric acid type carbonated drink, said member is sulfur and copper, and the content of said copper is always higher than that of said phosphorus

even in the case where the content of phosphorus is higher than that of sulfur.

5. The steel plate according to claim 1 wherein said member is 0.02 to 0.1% by weight of sulfur and 0.1 to 0.3% by weight of copper and the contents of said sulfur and copper are always higher than that of said phosphorus.

6. The steel plate according to claim 1 wherein the content of said manganese is 3 to 10 times as large as that of said sulfur.

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