PROCESS FOR DETINNING TINNED SHEET IRON

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Filed: Feb. 16, 1970
Appl. No.: 11,290

Foreign Application Priority Data
Feb. 20, 1969 Germany P 19 08 503 1

U.S. Cl. 75/98, 75/64
Int. Cl. C22b 25/06
Field of Search 75/64, 85, 98; 23/89, 152

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ABSTRACT
This invention relates to a process of detinning tin-plated sheet iron with soda lye in the presence of sodium chlorite as an oxidizing agent.

3 Claims, No Drawings
This invention relates to a process for detinning tin-plated sheet iron, i.e., tin-plate, with soda lye in the presence of an oxidizing agent.

In addition to the processing of tin ores, the recovery of tin from waste tin-plated sheet iron plays an important role in the production of tin metal.

For the purpose of recovering tin from tin-plate, three primary processes have been proposed to date, specifically:

a. the chlorine detinning process,

b. the electrolytic process in an alkaline medium, and
c. the removal of the tin with the aid of soda lye in the presence of a suitable oxidizing agent, with subsequent electrolytic separation of the tin.

Various compounds have been proposed as oxidizing agents for the removal of the tin with the aid of soda lye in the presence of an oxidizing agent such as, for example, alkali nitrite, alkali nitrate, alkali hypochlorite, alkali thiosulfate, and alkali polysulfide. This process is preferably employed in the case of high tin-plate quantities.

In this process, the tin which was applied to the iron galvanically or by hot-tinning as a superimposed layer during the tin-plating operation is removed as a result of the reaction of the soda lye in the presence of one of the aforementioned oxidizing agents, but not any tin which may be present in the form of an iron-tin alloy.

It has been found that tin may be removed from tin-plated sheet iron or iron plate in a particularly effective and rapid manner with soda lye containing an oxidizing agent when sodium chloride (NaClO) is employed as the oxidizing agent.

During the removal of the tin with soda lye in the presence of sodium chloride, if at least equimolar quantities of sodium chloride are present, tin is oxidized from the nonvalent state through the bivalent to the tetravalent state, while sodium chloride is reduced to sodium chloride. Formed at the same time is a soluble sodium hydroxy-stannate complex, but the iron is not attacked thereby and can be furnished, after detinning, to the steel industry as a valuable scrap, so-called "black plate." In this connection, it is of special significance that the residual tin content of the black plate is low if sodium chloride is employed as the oxidizing agent.

It is a particular advantage resulting from the use of sodium chloride, as proposed by the present invention, that detinning can be effected in an economical manner at elevated temperatures if equimolar sodium chloride quantities, based on the tin, are present in excess quantities of soda lye. The excess of soda lye, however, may be maintained lower than was the case with the oxidizing agents used heretofore.

The detinning operation preferably is performed at an elevated temperature in the range of about 50° to 100° C. Particularly preferred is the temperature range of 80° to 95° C.

When using excess quantities of soda lye and sodium chloride, it generally suffices to perform the detinning operation with only one detinning solution. An extensive detinning of the tin-plated sheet iron is effected by virtue of the effective detinning action in the presence of sodium chloride.

Since, in the process of the invention, it is possible to employ low lye concentrations, relatively large quantities of tin may be recovered with the relatively good solubility of tin in dilute soda lye, particularly if it is ensured that the soda lye and sodium chloride concentrations are continuously maintained in correspondence with the consumption thereof. Actually, however, the concentration of soda lye always should be so selected that excess quantities thereof are present, as compared to the lye concentration which is required as hydroxy-stannate for the complex formation of the tin.

Since the detinning of tin-plated sheet iron with soda lye in the presence of sodium chloride is particularly effective, detinning may be performed in shorter periods of time than was possible with the oxidizing agents heretofore employed, employing the same process conditions in both cases. Lacquered tin plate should be disassembled in known manner prior to the detinning thereof with sodium chloride-containing soda lye so that the sodium chloride-containing soda lye solution is fully effective.

It is preferable that either the tin-plate to be detinned have a rotary movement imparted thereto in a suitable vessel during the detinning operation or that the liquor be agitated and recycled. This ensures an intimate contact of the detinning lye with the tin-plate. If desired, air also may be passed through the liquor from below the tin-plate to be detinned.

Since, during the detinning of tin-plate with sodium chloride-containing soda lye, sodium chloride is obtained as a reduction product, it is desirable to separate the tin contained in the liquor, by means of a subsequent precipitation process, in the form of stannic acid and stannous hydroxide. The separated stannic acid either may be subjected to electrolysis, after washing and dissolving in soda lye, with a view toward metal recovery in the form of the stannate solution thereby obtained or, with a view toward the recovery of solid sodium stannate, it may be employed as sodium stannate solution for recovering the solid product. In principle, the liquors obtained during the detinning of tin-plate with sodium chloride-containing soda lye also may be directly fed to an electrolysis operation but, in such case, a certain corrosion of the anode material must be accepted due to the intermediate anodic formation of chlorine, and also of sodium hypochlorite and sodium chlorate, depending upon the temperature, as a result of an immediate secondary reaction.

If sufficiently long detinning times are used, especially low residual tin contents may be achieved in the black plate obtained from the process.

The particularly good detinning of tin-plate with the aid of soda lye in the presence of sodium chloride, as compared to heretofore known oxidizing agents, is further illustrated by reference to the following specific examples.

EXAMPLE 1

Approximately 150 grams of tin-plated sheet iron, containing 0.79 per cent by weight Sn, are placed into a cylindrical perforated iron drum, having a capacity of about 700 ml, which is rotatably mounted in an iron tank having a capacity of about 4 liters. The ratio of the perforated surface to the metallic surface of the iron drum is 1:6.8.

The mounting of the perforated iron drum is so maintained that about two-thirds of the surface thereof is immersed (during the rotation thereof at the rate of 4.5 revolutions/min.) in the liquor (about 320 ml) which is present in the iron tank.

The liquor, which contains 3 grams of NaOH/1 and 0.32 gram NaClO,/1, is heated, during the rotation of the perforated iron drum filled with tin-plate, to about 80° C. After approximately 20 minutes detinning time at a liquor temperature of 80° C., the detinning operation is complete.

The detinned sheet iron (black plate) has a residual tin content of 0.012 per cent by weight.

COMPARATIVE EXPERIMENTS

A. 150 grams of tin-plate, containing 0.79 per cent by weight Sn, are detinned, in the apparatus of Example 1, for 20 minutes at a temperature of 80° C. in a liquor containing 3 grams of NaOH/1 and 0.53 gram of NaClO,/1.

The detinned sheet iron (black plate) has a residual tin content of 0.51 per cent by weight.

B. 150 grams of tin-plate, containing 0.79 per cent by weight Sn, are detinned, in the apparatus of Example 1, for 20 minutes at a temperature of 50° C. in a liquor containing 5 grams of NaOH/1 and 2.0 grams of NaClO,/1.

The detinned sheet iron (black plate) has a residual tin content of 0.30 per cent by weight.

C. 150 grams of tin-plate, containing 0.79 per cent by weight Sn, are detinned, in the apparatus of Example 1, for 20 minutes at a temperature of 100° C. in a liquor containing 5 grams of NaOH/1 and 5 grams of NaClO,/1.

The detinned sheet iron (black plate) has a residual tin content of 0.40 per cent by weight.
EXAMPLE 2

Approximately 200 kilograms of tin-plate, containing 0.74 per cent by weight Sn, are introduced into a hexagonal perforated iron drum, having a capacity of about 1.5 m³, mounted in an iron tank having a capacity of about 4 m³. The ratio of perforated surface to metallic surface of the hexagonal perforated iron drum is 1 : 8.5.

A detinning liquor, which contains 3.4 grams of NaOH/l and 0.32 gram of NaClO₂/l, is heated to 85°C during rotation, at one revolution/min., of the perforated iron drum filled with the tin-plate.

During the rotation of the drum, about half of the drum is immersed in the liquor.

While air is simultaneously introduced below the drum, the detinning of the tin-plate is effected during 2 hours at a temperature of 85°C. The detinned sheet iron (black plate) displays a residual tin content of 0.048 percent by weight.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. In the process of detinning tin-plated sheet iron with excess soda lye, based upon tin, and in the presence of an oxidizing agent, the improvement which comprises employing sodium chlorite (NaClO₂) as the oxidizing agent, the sodium chlorite being present in at least equimolar quantities with respect to tin.

2. A process according to claim 1 performed at a temperature in the range of about 50°C to 200°C.

3. A process according to claim 2 in which air is passed through the reaction mixture.

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