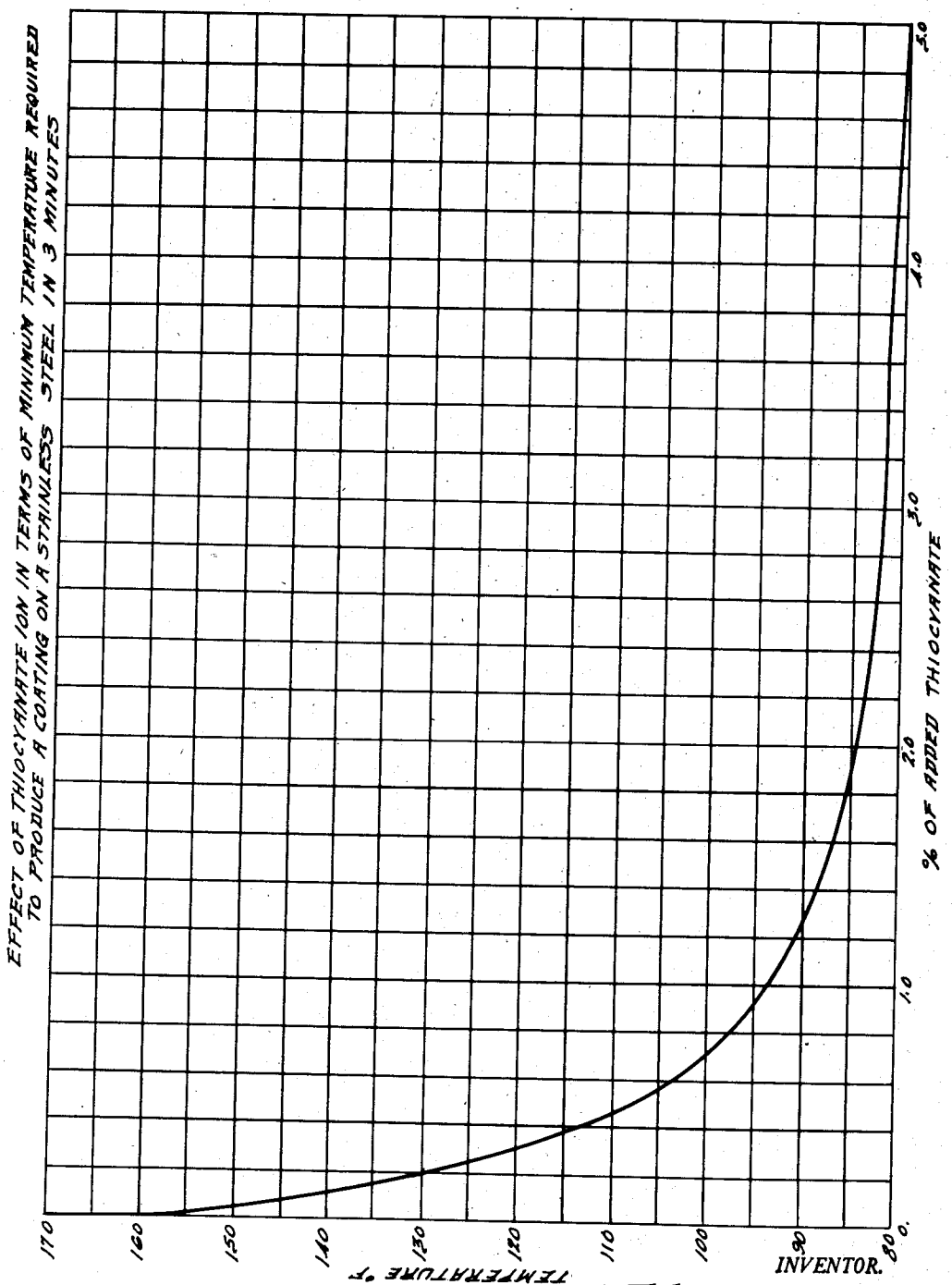
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SULFIDE COATING

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SULFIDE COATING

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4 Claims. (Cl. 148—6.24)

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This invention concerns a composition and method for the forming of sulfide coating on a steel surface, particularly on corrosion resistant and stainless steel surfaces.

This application is a division of prior copending application, Serial No. 138,251, filed January 12, 1950.

It is known that acid solutions of sulfites and certain other sulfur compounds can be used to attack the surface of a ferrous metal to form a sulfide coating thereon. These coatings may serve various functions. For example, in some cases they are used as a paint base and in some cases they are used as a protective coating for the metal when the latter is subjected to wear or to extensive plastic deformation as in drawing and the like. The coatings, because of their insolubility in acid solutions, are superior to phosphate and oxalate coatings in those uses which require contact of the coating with oils of high acidity.

In order to form such a coating, it is necessary that the solution attack the surface of the metal and form a salt of the metal. It has been pointed out, however, that the acid should not be sufficiently strong to cause excessive pickling of the metal since such pickling action, if too energetic, will prevent the forming of a coating. Therefore, it has been the practice to limit the acidity of the solution and to increase the rate of attack of the solution on the metal to the point desired by a suitable increase in the solution temperature.

The problem of securing both adequate and a controllable attack of the acid on the metal surface has been accentuated in the case of stainless steels which are normally quite resistant to acid attack. The forming of sulfide coatings on such normally resistant metal surfaces is usually carried out at temperatures near the boiling point of water, and, at best, in the range of 170° F.–200° F. Therefore, the process has been subject to all the disadvantages of high temperature operation; particularly the high vapor pressure of the treating solution and the difficulty of handling acid solutions at such temperatures.

It is an object of this invention to provide a solution and a method for the forming of a sulfide coating on the surface of a steel object, particularly on a corrosion resistant or on a stainless steel object.

A further object is to provide a strongly acid composition for the treatment of a steel surface to form a sulfide coating thereon while avoiding the excessive pickling effect normally encountered with such compositions.

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It is a further object to form a sulfide coating on a steel surface, particularly corrosion resistant and stainless steel surfaces, at temperatures much lower than those used heretofore.

I have now found that the foregoing and related objects can be secured by subjecting the surface of the steel to the action of an acidic aqueous solution comprising as essential ingredients the sulfide ion or compounds capable of yielding the sulfide ion at said steel surface; the thiocyanate ion; and a proportion of an acid sufficient to provide a pH below about 1.1.

Preferred compositions include the sulfite ion; but sulfide, thiosulfate, reducible organic sulfur-containing ions, etc., may be used. All such ions, other than the sulfide ion itself, form sulfide ions at the metal surface through reduction by the metal.

The drawing illustrates graphically, the effect of the addition of thiocyanate in lowering the temperature required to produce a satisfactory coating on an 18–8 stainless steel in an arbitrarily selected short period of time. The time chosen is three minutes. The curve represents addition of thiocyanate to a 5% sulfuric acid solution containing 0.32% sulfite ion.

As shown in the graph, the 5% sulfuric acid solution containing 0.32% sulfite ion produces a satisfactory three-minute coating at about 165° F. Extremely small proportions of thiocyanate ion effect a marked reduction in the temperature required for such a three-minute coating. This curve was determined by a large number of individual determinations, and is typical of those obtained with a variety of acids and a variety of sulfide ion producing materials.

I have found that two limitations, that is, the degree of acidity and the presence of thiocyanate ion are necessary to the obtaining of a successful result. If the pH of the solution is higher than about 1.1 the addition of the anion has little advantage. Where, however, the pH of the solution is less than about 1.1, even very small percentages of the thiocyanate ion have a marked effect; especially in the lowering of the temperature required for the formation of an effective coating in a reasonably short time. For example, as little as about .05% thiocyanate has a marked effect on the temperature required where the acidity is less than a pH of 1.1 as may be seen in the drawing.

The lower limit of pH is not critical and depends somewhat on the particular acid chosen,

the concentration of the thiocyanate ion, the degree of pickling action produced, the particular steel being coated and the degree of pickling which can be tolerated for the type of coating desired. However, it may be stated as a general rule that the pH range to be used is from 0.3 to 1.1. No particular advantage is gained by operating at the extreme limits of acid concentration since the entire advantage of the invention can be obtained when the pH is less than 1.1 and substantially above 0.5. If, however, it be desired to operate at the lowest possible pH, it is a matter of a few simple tests to establish the lower limit permissible with the particular steel and the thiocyanate ion.

The sulfite ion concentration is normally maintained at about 0.3 to 1.3% but this proportion has been varied over relatively wide limits. It is preferred that the thiocyanate ion be maintained above about 1% in order to secure the maximum benefits from the invention, but some advantage can be gained with very minor percentages. Highly concentrated solutions, up to saturation, of the various ions can be used but little advantage is gained above 1.3% sulfite or about 5% of thiocyanate ion.

The particular acid selected is not important except that it is strong enough to provide the required pH. The mineral acids are both stronger and inexpensive as compared with other acids, e. g., benzene sulfonic and trichloracetic, and hence are preferred. Sulfuric, hydrochloric and nitric acids are especially preferred. Acids which are not sufficiently strong to give the desired pH may be used if a suitable proportion of a stronger acid is used in the same composition. Similarly the source of sulfite, thiocyanate, etc., is not important provided the cation provided with said ion be compatible with the solution; that is, not precipitate out an essential ingredient or have any other adverse effect on the solution or the coating.

The metals treated comprise the entire category of steels including mild steels, corrosion resistant, and stainless steels and, as pointed out previously, the invention has particular advantage in treating stainless steels because of the avoidance of the high temperatures normally required in their coating. The coatings produced are salts of the metals treated and vary somewhat with different alloys. Certain of the metals encountered in alloy steels have a tendency to form an oxide rather than a sulfide and, therefore, the average coating contains some oxide. Nickel appears to be particularly active toward the compositions of the invention and nickel steels usually produce a high percentage of nickel sulfide in the coating.

The following examples are given to more clearly illustrate the method and solutions of the invention:

Example 1

A solution was made up containing 10 grams of sodium sulfite per gallon of water and containing 20 cc. of 95% sulfuric acid, the solution having a pH of 1.1. A temperature of 200° F. was required to produce a coating on the stainless steel in three minutes.

Example 2

A series of solutions containing 5% sulfuric acid and 0.32% sulfite was made up. Each of

the solutions contained successively the following thiocyanate percentages: 0.0, 0.1, 0.3, 0.5 and 5.0%. In the solution containing no thiocyanate, a coating was produced in three minutes at 157° F. on stainless steels. In the remaining solutions containing .1 to 5% thiocyanate, a satisfactory coating was obtained in three minutes at 140°, 125°, 105° and 80° F., respectively.

Although I do not wish to be limited by theory, I believe that the thiocyanate ion has an activating influence on the acid attack on the metal. This permits a suitable and controlled attack at a lower temperature for the purpose of forming a coating on the metal. It appears also that the activation does not significantly increase the pickling effect, but in some cases, may reduce this effect when full advantage is taken of the lowered coating temperature. As indicated previously, the invention permits of a more rapid coating of stainless and corrosion resistant steels and is particularly advantageous in this respect.

What is claimed is:

1. A composition for forming a sulfide coating on a steel surface which consists essentially of a member of the group consisting of the sulfide ion and ions which form the sulfide ion through reduction on the steel surface and in a proportion equivalent to about .3 to 1.3% sulfite ion, the thiocyanate ion in a proportion of from .05% up to and including saturation, and an acid selected from the group consisting of sulfuric, hydrochloric and nitric in a proportion sufficient to provide a pH in the range of about .3 to 1.1.

2. A composition for forming a sulfide coating on a steel surface which consists essentially of a member of the group consisting of the sulfide ion and ions which form the sulfide ion through reduction on the steel surface and in a proportion equivalent to about .3% to 1.3% sulfite ion, the thiocyanate ion in a proportion of from 1% to 5%, and an acid selected from the group consisting of sulfuric, hydrochloric and nitric in a proportion sufficient to provide a pH in the range of about .3 to 1.1.

3. The method of forming a sulfide coating on a steel surface which comprises contacting the surface with a solution consisting essentially of the sulfide ion and ions which form the sulfide ion through reduction on the steel surface and in a proportion equivalent to about .3% to 1.3% sulfite ion, the thiocyanate ion in a proportion of from .05% up to and including saturation, and an acid selected from the group consisting of sulfuric, hydrochloric and nitric in a proportion sufficient to provide a pH in the range of about .3 to 1.1.

4. The method of forming a sulfide coating on a steel surface which comprises contacting the surface with a solution consisting essentially of the sulfide ion and ions which form the sulfide ion through reduction on the steel surface and in a proportion equivalent to about .3% to 1.3% sulfite ion, the thiocyanate ion in a proportion of from 1% to 5%, an an acid selected from the group consisting of sulfuric, hydrochloric and nitric in a proportion sufficient to provide a pH in the range of about .3 to 1.1.

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No references cited.