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METHOD OF PROTECTING METALS AGAINST ELECTROCHEMICAL CORROSION OF THE ACIDIC TYPE

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This invention relates to a method for protecting metals against electrochemical corrosion of the acidic type; i.e. corrosion due to an acidic medium and resulting in liberation of hydrogen. It is noticeable that the corrosion due to an acidic and simultaneously strongly oxidizing medium is not of the acidic type since no hydrogen is evolved during the corrosion process. This is the case especially when nitric acid is the acidic medium or the main acidic component thereof. On the contrary perchloric acid as well as sulfuric and hydrochloric acids acts as a corrosive agent of the acidic type since the corrosion process in perchloric acid medium results in hydrogen liberation.

It is an object of my invention to provide a method for the protection of metals against electrochemical corrosion of acidic type which inhibits this corrosion several times better than the known anti-corrosive agents.

It is a well-known fact that the electrochemical corrosion of metals such as iron, steel, and the like, is particularly strong in acidic media. Till now, the known anti-corrosive agents have frequently been unsatisfactory when used against this particular type of corrosion.

Different types of anti-corrosive agents have been used among which there shall be mentioned, as examples:

Long chain aliphatic fatty acids having from 8 to 24 carbon atoms per molecule and their salts, such as oleic acid, sodium laurate, potassium stearate and the like.

Sulfonic acids and their salts, such as anthraquinone β-sulfonic acid, sulfonated mineral oils, alkylated naphthalene sodium sulfonates and the like.

Primary, secondary and tertiary aliphatic amines, where the different hydrocarbon radicals have from one to 20 carbon atoms, such as amylamine, hexylamine, cyclohexylamine, dodecylamine, tetradecylamine, octadecylamine, dimethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, dicyclohexylamine, didodecylamine, trimethylamine, triethylamine, tripropylamine, triamylamine, trihexylamine, ethylmethylamine, ethylenediamine, triethanolamine, hexamethylenetetramine, and their acid addition salts such as sulphates, hydrochlorides, acetates and the like.

Primary, secondary and tertiary aromatic amines such as o., m. and p. toluidines, o. xylidine, 2,6-xylidine, 3,5-xylidine, m. ethylaniline, m. propylaniline, m. butylaniline, α-naphthylamine, pheneylenediamine, methylaniline, ethylaniline, propylaniline, dimethylaniline ethylmethylaniline, diethylaniline, dibutylaniline and the like.

Heterocyclic nitrogenated compounds of aliphatic nature such as morpholine, phenylmorpholine, ethanol morpholine, imidazolines, aminoalcoylimidazolines, or of aromatic nature such as pyridine, picoline, collidine, lutidine, 3-ethylpyridine, 3-propylpyridine, 3-butylpyridine, quinoline, acridine and the like.

Quaternary ammonium salts such as betaine, dodecyltrimethylammonium chloride and the like.

Amides and thioamides such as thiourea, phenylthiourea, o. and p. tolylthiourea and the like.

Hydrazines such as phenylhydrazine and the like.

Phenols and thiophenols such as thiophenol, o., m. and p. thiocresols, 2-thionaphtol and the like.

Mercaptans, where the hydrocarbon radical comprises

from 2 to 20 carbon atoms, such as ethylmercaptan, propylmercaptan, butylmercaptan, isobutylmercaptan, tertiobutylmercaptan, amylmercaptan and the like.

Sulfides and disulfides having, respectively, the general formulae:

R—S—R′ and R—S—S—R′

wherein R and R′ are hydrocarbon radicals either identical or differing from each other, preferably of aliphatic type, and containing from 1 to 20 carbon atoms per radical, and for example methylsulfide, ethylsulfide, propylsulfide, butylsulfide, butylmethylsulfide, propyldisulfide, butyldisulfide and the like.

Aldehydes such as formaldehyde, acetaldehyde, proprionaldehyde, butyraldehyde, crotonaldehyde, benzaldehyde, o., m. and p. tolualdehydes and the like.

Ketones such as diethylketone, dipropylketone, diisobutylketone, butylmethylketone, isobutylmethylketone, tertiobutylmethylketone, amylmethylketone, ethylpropylketone, acetonylacetone, pinacolone, phorone, cyclohexanone, acetophenone, propiophenone, butyrophenone, valerophenone and the like.

Esters such as n-octylsulfate, dodecylsulfate and the like.

Ethers such as cineol and the like.

Sulfones such as butylsulfone and the like.

Selenides such as ethylselenide and the like.

Such anti-corrosive agents are described for instance, in "The Corrosion Handbook," by H. H. Uhlig, John Wiley & Sons, New York (1948).

While these inhibitors permit to reduce to a certain degree the intensity of electrochemical corrosion of the acidic type taking place at the surface of metals such as iron or steel, this corrosion remains nevertheless too high to permit a truly effective protection of the metal against corrosion under really severe conditions of use of the same.

Among the conditions which are particularly liable to provoke a strong corrosion of the acidic type at the metal surfaces, there is known to be the presence of elementary sulfur in suspension in an acidic medium. I have carefully studied this corrosion-augmenting effect of finely, for instance, colloidally suspended sulfur on metal surfaces in acidic medium, and have found that even extremely small amounts of sulfur have a high corrosion-intensifying activity.

Experiments carried out by me consisted in immersing a strip of iron having a surface of 30 square centimeters for 24 hours into 500 ccs. of an aqueous $\frac{1}{100}$-normal hydrochloric acid solution at room temperature, and to measure the loss of weight of the strip due to corrosion, then to repeat the experiment, each time with a fresh strip of the same iron, with the aforesaid HCl-solution to which varying very small amounts of sulfur had been added in the form of a colloidal suspension obtained by adding to the diluted acid each time 20 ccs. of a sulphur solution in ethyyl alcohol as the solvent. The results of these experiments are given below in Table I.

TABLE I

Content of sulfur in the HCl-solution in parts per million by weight (p.p.m.)	Weight loss of iron strip in milligrams (mg.)
0	38.2
5	143.8
13	169.5
26	224.1
52	237.0

These experiments show the increase in the corrosive activity of hydrochloric acid solution of the above-stated HCl-concentration when containing the above very small amounts of sulfur. The chemical causes of this increase in corrosive activity are not well known. However, the above experiments lead me to assume that the increased corrosive activity is not due to the presence of sulfur in suspension in the acidified water, but to sulfur atoms fixed in some manner, perhaps by adsorption or otherwise, on the metallic surface. The action of these sulfur atoms is believed to be purely catalytic for they are not used up during the corrosion process as the following experimental tests have shown.

Test A

A soft steel strip having a surface of 30 cm.^{2} and determined weight (the exact composition of the steel is immaterial as long as the same steel is used for all comparative tests) is polished electrolytically in a known manner and then immersed at 20° C. in a solution of benzene containing 1% by weight of sulfur, then withdrawn, washed three times with pure benzene, and then immersed for 5 minutes in pure benzene, washed again, dried and weighed.

Only sulfur atoms chemically adsorbed or fixed by another chemical phenomenon can remain on the metal surface. Weighing was carried out with a balance having a sensitivity limit of 0.1 milligram. No noticeable increase of the weight of the steel strip was found, the amount of sulfur atoms fixed on the metal, if any, was thus below 0.1 milligram.

Test B

A strip thus prepared is then immersed in an aqueous hydrochloric acid solution containing 10% by weight of HCl. After 48 hours' immersion the strip is removed, dried and weighed and shows a loss, due to corrosion, of 136.2 milligrams.

Test C

A strip of identical material, dimensions and weight is immersed, without having previously undergone the treatment of test A, in the same kind of aqueous hydrochloric solution as used for test B, i.e. with a concentration of 10% by weight of HCl. After 48 hours, the strip is removed, dried and weighed, and shows a weight loss of only 75.4 mg.

These tests B and C show that the lighter weight loss due to corrosion in the former test surpassing by 60 milligrams the weight loss in test C is caused by the assumed presence, on the steel surface, of sulfur atoms in a total amount of less than 0.1 milligram. The sulfur must thus act catalytically.

Further experiments carried out by me using acidic solutions of varying pH, have revealed that the increase of corrosive activity of the acidic type imputable to the presence of sulfur above the normally determined corrosive activity is the stronger, the higher the acidity of the corroding liquid.

Further tests D to H were, therefore, carried out by me each consisting in preparing a corrosive liquid from de-aerated water saturated with hydrogen sulfide and adjusted to various pH values by the addition of first hydrochloric acid and then partial neutralization with sodium hydroxide, while retaining the concentration of chlorine ions in the resulting solutions constant in all solutions; and then immersing for 2 hours 30 minutes on the one hand, steel strips of the same type, dimensions and weight as used in tests A–C that were previously polished electrolytically, and, on the other hand, strips of the same kind, treated additionally as described in test A supra. The corrosive liquid was caused to circulate at a velocity of 15 centimeters per second past the strips.

The results of tests D to H are given in Table II:

TABLE II

Test No.	pH of aqueous acidic solution	Steel strip not treated by Test A	Steel strip treated by Test A (less than 0.1 mg. of S)	Percent increase due to S
D	5.4	9.3	11.6	25
E	4.9	12.0	14.3	19
F	3.8	15.3	21.2	38.5
G	3.0	16.6	25.0	50.8
H	1.8	18.6	35.3	89.6

These results show that, while at pH values about 5 the increase in corrosion due to the presence of very small amounts of catalytically active sulfur that must be assumed on the steel surface, is in the order of 20–25%, the increase in corrosion at pH values between 3 and about 1.8, the increase due to what must be assumed to be substantially the same amounts of sulfur, is from about 50 to 90%.

This increased corrosive activity is not only limited to losses in weight of the metal but also brings about blisters and cracks in the metal surface due to the penetration into the metal of hydrogen, generated during the corrosion process, of the acidic type.

Contrary to what would have to be expected from the above experiments, I have discovered that in spite of the strong corrosion-enhancing activity of sulfur in acidic solution, the same sulfur will surprisingly enough, strongly enhance the anti-corrosive activity of substances conventionally known as anti-corrosive agents in acidic media, and will also protect or help to protect the metal against the penetration of hydrogen evolved during the corrosion process of the acidic type.

The method according to the invention therefore comprises adding to an acidic corrosive liquid, predominantly an aqueous acidic solution, having a corrosive action of the acidic type, such as solutions of hydrochloric acid, sulfuric acid, perchloric acid, carbonic acid, sulphhydric acid, or organic acids such as acetic acid, butyric acid, benzenesulfonic acid and the like, a known anti-corrosive agent for acidic media such as that hereabove mentioned, in conventionally used amounts, which agent is preferably selected from the group consisting of the most usual commercial anti-corrosive agents which are generally constituted on the basis of primary, secondary, and tertiary aliphatic amines, quaternary ammonium salts derived from the latter amines, cyclic amines such as piperidine, morpholine and imidazolines and organic sulfides and disulfides having, respectively, the formulae R—S—R′ and R—S—S—R′, wherein R and R′ are hydrocarbon radicals either identical or different from each other, preferably of aliphatic nature, and containing from 1 to 20 carbon atoms per radical; and further adding to the solution, preferably in the form of a solution in ethyl alcohol, gasoline, benzene, carbon disulfide, finely dispersed sulfur to form in the liquid a preferable colloidal suspension of the latter, in such amounts that a significant increase of the anti-corrosive activity of the known anti-corrosive agent is achieved. The conventional proportions of anti-corrosive agent in the corrosive acidic medium extend usually within a wide range according to economic considerations.

In most cases and up to a maximum concentration far outside the usual economic range, the higher is the concentration of anti-corrosive agent in the corrosive medium, the lower is the corrosion intensity. However, since the anti-corrosive agent can hardly be recovered from its solution in the corrosive medium and is consequently lost when fresh corrosive medium is continuously circulated in contact with the metal, it is generally appropriate for economic reasons to limit the proportion of such anti-corrosive agent to the minimum quantity which secures

a sufficient protection to reduce the corrosion intensity to an acceptable level. This minimum quantity may be reduced considerably according to the present invention, due to the action of sulfur in cooperation with said anti-corrosive agent. However it is necessary that in any case the proportion of anti-corrosive agent in the corrosive medium be at least equal to that proportion for which the use of the anti-corrosive agent alone, i.e., without sulfur, is effective by carrying out a testable reduction of the corrosive intensity. This minimum proportion is conventionally known in the art for each known anti-corrosive agent. In most cases it is of the order of 5 to 10 parts per million by weight. Usual range of concentrations used is from 5 to 100 parts per million by weight. In the case of anti-corrosive agents of relatively low activity a technical improvement resulting in a lowering of the corrosive action may still be achieved by the use of higher concentrations of the anti-corrosive agent, for example up to 1000 parts per million by weight, but economic considerations do not permit, except perhaps in some very particular cases, to assume so high expenses in order to achieve a relatively slight improvement of the protection of the metal as compared to that obtained with the same or other anti-corrosive agents used at lower concentrations of from 5 to 100 parts per million by weight. It must be noted that such concentrations are of the catalytic type, i.e. have no effect on the pH of the corrosive medium.

For carrying out the present invention such concentrations of from 5 to 100 p.p.m. of anticorrosive agents are preferably used and most particularly the lowest concentrations for which a still significant reduction of the corrosive action of the corrosive medium is achieved.

To the corrosive medium containing said proportion of anti-corrosive agent is added, according to the invention, finely divided elementary sulfur. The amounts of sulfur to be used may be as low as wanted and very low proportions are proved to be sufficient to enhance to a large extent the anti-corrosive activity of the inhibitor. Since the cost of sulfur is not too high, larger amounts than that just sufficient may be used. However too high proportions are not recommended since it has been observed that beyond a certain optimal proportion dependent mainly in each case on the nature of the corrosive liquid medium, the corrosive action of the latter increases again and for very high concentrations becomes even greater than in the absence of both anti-corrosive agent and sulfur. The amounts of sulfur thus required can be determined from case to case empirically and without great difficulty, as demonstrated hereinafter in the examples using various types of acidic media.

According to another important feature of my invention the elementary sulfur introduced or formed in the acidic solution and brought into contact with the metallic surface to be protected should have an average particle size of less than 500 microns and preferably less than 100 microns. No lower limit of that size has been observed and the process according to the invention may be carried out by using particules of the smallest size available or even sulfur in the state of a true solution in the corrosive medium (which may be for instance the case when the corrosive medium contains significant proportions of sulfuric acid).

Depending on these two factors, a preferred range of sulfur concentration in the corrosive liquid containing the known anti-corrosive agent can be found, which range corresponds to a significant increase of the anti-corrosive activity of the agent.

Since the anti-corrosive effect of the mixture varies progressively as a function of the amount of sulfur fixed on the metal surface and of the concentration of anti-corrosive agent in the liquid, it is easy to determine with satisfactory precision the limits of the aforesaid range of optimal anti-corrosive increase from case to case. Said range is always wide enough to permit satisfactorily the

use of the invention process without being necessary to determine the optimal proportion of sulfur. Even if the proportion of sulfur is too high a significant improvement of the anti-corrosive activity of the agent is nevertheless obtained.

In most cases one can use as "starting proportion" 30 parts per million for example, and observe thereafter if the anti-corrosive activity of the agent increases or diminishes when a higher proportion is employed.

In the case of an increasing activity a higher proportion may advantageously be used, if the supplemental resulting cost is deemed acceptable. On the contrary if a reduction or the maintenance of the anti-corrosive activity of the agent is to be observed, a lower proportion such as for instance 10 parts per million must be tested at least for economic reasons and if again at this latter concentration the corrosive activity of the liquid medium is still unchanged or is lower, concentrations of, for example, 3 parts per million or less should be used.

Accordingly the usual range of sulfur concentrations in the acidic-corrosive medium extends from 0.5 to 100 parts per million by weight. However it suffices to have a certain amount of sulfur adsorbed on the metal surface and this amount always corresponds to a concentration which is far lower than 0.5 part per million. Consequently I do not wish to limit myself to the use of proportions of sulfur higher than 0.5 part per million. On the contrary my experiments prove that for any given proportion of the anti-corrosive agent, very low concentrations of sulfur have still an enhancing effect.

In the case of an aqueous solution of hydrogen sulfide containing tetradecylamine at a concentration of 10 p.p.m., a sulfur concentration of 20–25 p.p.m. in the corrosive liquid will bring about optimal reduction of the corrosion effect, namely, to about one fourth of the corrosion still suffered by the metal when tetradecylamine alone is present in the corrosive liquid. This is a strong indication that there is in fact a synergistic action between the tetradecylamine and the sulfur in the liquid.

If the concentration of tetradecylamine in that corrosive medium is 20 p.p.m. optimal results will be obtained with a concentration of sulfur in the range of 80 to 100 p.p.m. It is quite remarkable that a slightly lower as well as a slightly higher sulfur concentration below and above the aforesaid range will leave only an anti-corrosive activity several times inferior to that achieved by the presence of sulfur in the aforesaid concentration range.

Therefore, within the characteristic range depending on the prevailing concentration of sulfur and anti-corrosive agent in the corrosive liquid, the presence of sulfur, instead of favoring the corrosion, as was to be expected, permits to augment several times the anti-corrosive activity of agents of the above-mentioned group, and this to such a degree that the combined use of sulfur and the known anti-corrosive agent permits to practically eliminate the corrosion of the metal over long periods of time.

The anti-corrosive effect-enhancing property of sulfur in the described concentration range is particularly surprising in view of the corrosion-enhancing properties of the same sulfur described in detail hereinbefore in connection with Tests A–H, and I have at present no scientific explanation for what I have termed for want of a better explanation, a synergistic phenomenon.

I wish to state again that an anti-corrosive protection accorded to metal surfaces in acidic corrosive media by the combined use of a known anti-corrosive agent of the class described and sulfur which is in effect very considerably higher than that achieved with the known agent alone, can only be attained if the amount of sulfur used is carefully adapted to the nature of the acidic medium having a corrosive action of the acidic type on the metal surface to be protected and is in a determined suitable ratio to the amount of known anti-corrosive agent present; otherwise the remarkable increase of the anti-corrosive effect of the combination cannot be realized.

The examples given hereinafter permit to show in more detail the ranges of sulfur amounts necessary in order to obtain optimal anti-corrosive protection, and serve to illustrate the invention without being in any way or form considered as limitative of the scope of the same, "p.p.m." in these examples means always parts by weight per million.

Example I

To 100 liters of a metal-corrosive liquid consisting of $\frac{1}{10}$ normal aqueous hydrochloric acid solution there are added 1 gram of tetradecylamine and 100 ccs. of ethyl alcohol containing dissolved 0.5 gram of sulfur. The resulting mixture contains approximately 10 p.p.m. of the anti-corrosive agent and about 5 p.p.m. of colloidal sulfur.

Example II

Example I is repeated, but 200 ccs. of the sulfur-containing ethyl-alcoholic solution are added instead of the amount used in the preceding example.

Example III

Example I is repeated, but 500 ccs. of the sulfur-containing ethyl-alcoholic solution are added to the mixture.

Strips of soft steel of identical composition and dimensions are subjected to a known electrolytic polishing treatment followed by an equally conventional reducing treatment in a hydrogen atmosphere at 500° C.

The strips are then immersed in different aqueous $\frac{1}{10}$ normal solutions of hydrochloric acid. Sulfur is introduced into these solutions in colloidal form by adding to the same corresponding amounts of a solution of the sulfur in ethyl alcohol, so as to obtain a sulfur concentration in the HCl-solutions of 5, 10 and 25 p.p.m. respectively. Each of the solutions contains, as inhibitor, 10 p.p.m. of tetradecylamine. Immersion of the strips lasts for 48 hours and is carried out at room temperature. The results showing weight losses expressed in milligrams per square decimeter of surface and per day, are tabulated in Table III below:

TABLE III

	Corrosive liquid (1/10-N HCl in H_2O)				
	Without anti-corrosive agent and sulfur	With 10 p.p.m. tetradecyl-amine	With 10 p.p.m. tetradecyl-amine and colloidal sulfur in amounts of—		
			5 p.p.m.	10 p.p.m.	25 p.p.m.
Weight loss in mg./dm.² per day	282	120	37	31	30

Table III shows clearly that the use of only 25 p.p.m. of sulfur makes the anti-corrosive agent, tetradecylamine, in the same concentration of the latter, four times as effective as when used without sulfur.

Example IV

Example I is repeated, but instead of the amount of sulfur-containing alcoholic solution used therein, 40 ccs. of the latter are added to the HCl-solution.

Tests with the acidic solutions prepared according to Examples I and IV were carried out after saturating the solutions with oxygen. The subsequent Table IV shows the results of corrosion tests lasting for 48 hours, with the same kind of testing strips as used in the previous tests, losses of weight being stated in mg./dm.² per day.

TABLE IV

	Corrosive liquid containing 1/10-normal HCl in H_2O			
	No inhibitor and no sulfur	10 p.p.m. of tetra-decylamine	10 p.p.m. of tetradecylamine and colloidal sulfur in concentrations of—	
			5 p.p.m.	20 p.p.m.
Weight loss in mg./dm.² per day	325	300	63	56

This table shows that in the case of oxygen-saturated acidic corrosive liquids, the anti-corrosive effect of tetradecylamine in the given concentration is almost negligible, while the presence of small amounts of sulfur increases that effect by approximately five times.

Example V

To a corrosive liquid consisting of a mixture of 10 parts by weight of commercially available standard gasoline and one part by weight of an aqueous $\frac{1}{100}$ normal hydrochloric acid solution containing dissolved 35 milligrams per liter of hydrogen sulfide, there are added 10 p.p.m. of "Norust C 50," a commercially available anti-corrosive agent on an amine basis manufactured by Prochinor (Neuilly-sur-Seine, France). Sulfur is introduced into the liquid by adding thereto 2 p.p.m. in the form of a solution of sulfur in gasoline. The resulting liquid is substantially free from noticeable corrosive effects on surfaces of steel or iron for much longer periods of time than when using known anti-corrosives.

Comparative tests were carried out with this liquid as well as with liquid samples containing no sulfur and anti-corrosive agent and other samples containing only the latter agent. These tests were effected in the same manner as the preceding ones, but by immersion of the testing strips in the liquid for 12 hours at a liquid temperature of 40° C. The measured corrosion intensities expressed in mg./dm.² per day are given in Table V below:

TABLE V

	Corrosive liquid as described in Example V containing—		
	No anti-corrosive agent and no sulfur	10 p.p.m. of "Norust C 50"	10 p.p.m. of "Norust C 50" and 2 p.p.m. of colloidal sulfur
Weight loss in mg./dm² per day	1,580	338	9

These tests reveal a truly remarkable increase in the anti-corrosive effect of the "Norust C 50" agent, although the latter alone has already the effect of decreasing the corrosion to about one fifth. The presence of the small amount of sulfur brings about a more than 30 times stronger anti-corrosive effect of the same agent than is attained without sulfur.

A particularly noticeable feature is the presence of sulfide ions in the corrosive liquid. It is thus shown that the presence of colloidal sulfur is required in the liquid to bring about the above-described extraordinary anti-corrosive effect.

Example VI

To a corrosive liquid held under a pressure of 25 to 30 kilograms per square centimeter and consisting of a solution of hydrogen sulfide in de-aerated water in a concentration of about 60 grams per liter of H_2S, there are added 20 p.p.m. of tetradecylamine as anti-corrosive

agent and 90 p.p.m. of sulfur in the form of a benzenic solution of S.

An emulsion results which flocculates gradually on the surface of a metallic object introduced into the solution, and permits the fixation of sulfur on the metal surface.

Tests were carried out by preparing the above-described acidic solution in a steel autoclave, and then suspending in the solution several soft-steel strips electrolytically polished as described hereinbefore, and moving these strips so that they are subjected alternatingly to the action of the corrosive solution and to that of the vapor phase above the solution in the autoclave, pressure in the vapor phase varying between 25 and 30 kg./cm.^{2}.

Each test was carried out for a month. During this test period, no further anti-corrosive agent or sulfur was added. Comparative tests with the same acidic solution containing neither tetradecylamine nor sulfur had to be interrupted after three hours, and tests with the same corrosive solution containing tetradecylamine but no sulfur had to be interrupted after 24 hours, in both cases because there was danger of rupture of autoclave wall due to corrosion.

The test results are given below in Table VI; measured in the diminution of the thickness of the soft steel strips calculated in millimeters per year:

TABLE VI

Test No.	Temperture ° C.	Corrosive solution of H_2S in H_2O			
		Concentration of H_2S in g./liter	Without anticorrosive or sulfur	With tetradecylamine 20 p.p.m.	With 20 p.p.m. tetradecylamine and 90 p.p.m. of sulfur
			Reduction of strip thickness in mm./year		
K	40	57	2.5	0.46	0.01
L	80	38	4.5	0.56	0.06
M	110	30	----------	0.64	0.11
N	140	25	----------	0.73	0.19
			Penetration of hydrogen into strip	Penetration of hydrogen into strip	No penetration of hydrogen

This table again shows that always when sulfur is present in a ratio of tetradecylamine:S of about 1:4 to 1:5, corrosion of steel strips can be limited to a degree far below that attainable with the known anti-corrosive agent alone. An effective long-time protection against cracking of a steel autoclave by penetration of hydrogen through the corroded surface of the autoclave can be achieved even under severely adverse conditions of temperature and pressure, which protection cannot be attained with any known agent.

Example VII

To the same corrosive liquid as used in Example VI, there are admixed 20 p.p.m. of tetradecylamine, and 40 p.p.m. of sulfur in the form of a benzenic solution of S.

Example VIII

Example VII is repeated but the benzenic sulfur solution is added in such amounts that the sulfur content of the liquid is 80 p.p.m.

Example IX

A substantially non-corrosive acidic solution containing 90 p.p.m. of sulfur is prepared similar to the manner described in Examples VII and VIII.

Example X

An acidic solution containing 100 p.p.m. of sulfur is prepared similar to the manner described in Examples VII and VIII.

Example XI

An acidic solution containing 130 p.p.m. of sulfur is prepared similar to the manner described in Examples VII and VIII.

Example XII

Finally, an acidic solution containing 300 p.p.m. of sulfur is prepared similar to the manner described in Examples VII and VIII.

The amount of anti-corrosive agent in the aforesaid solutions of Examples VII to XII is always the same, but the weight ratio of this agent to colloidal sulfur in these solutions varies from 1:2 to 1:15.

Corrosion tests were carried out by immersing the same above-described kind of metal strips into these solutions under the conditions described in the tests made with the solution of Example VI and at a temperature of 80° C., and the results which have been compiled in Table VII below, clearly indicate the optimal range of the anti-corrosive agent: sulfur ratio which is between 1:4 and 1:5 for corrosive solutions containing 20 p.p.m. of tetradecylamine.

Corrosion is again measured by the diminution of the thickness of a test soft-steel strip, calculated in millimeters per year.

TABLE VII

Solution of Example No.	Concentration of S in p.p.m.	Diminution of strip thickness in mm./year
	0	0.56
VII	40	0.30
VIII	80	0.10
IX	90	0.06
X	100	0.09
XI	130	0.45
XII	300	2.7

The table shows that there exists in fact a rather well delimited range of the aforesaid ratio, above and below which, i.e. with less or more sulfur for one and the same content of anti-corrosive agent in the corrosive solution, the protection effect of the sulfur is lower, while in the above-mentioned optimal range this protective effect is five to ten times better than when exclusively using the anti-corrosive agent and no sulfur.

It is also noteworthy that in the presence of about seven times more sulfur than tetradecylamine there is practically no protection-increasing effect of the sulfur noticeable, i.e. the activity of the anti-corrosive agent is such as if no sulfur at all were present, and with higher sulfur contents the detrimental corrosion-enhancing effect of finely distributed elementary sulfur in acidic corrosive liquids comes fully into play.

Example XIII

Example VI is repeated with the same concentration of tetradecylamine and sulfur and a content of 38 grams per liter of hydrogen sulfide, but adding carbon dioxide gas to the solution in the autoclave at a rate of 8 grams per liter.

The same test as tabulated under No. L in Table VI is then repeated at 80° C. and under a pressure of 50 kg./cm.^{2}. The test soft-steel strip is reduced in thickness by the rate of only 0.1 millimeter per year.

Example XIV

A soft steel strip of 50 x 30 x 0.5 mm. is annealed in pure hydrogen at 800° C. for 3 hours and let cooled down to room temperature in hydrogen atmosphere.

This strip is weighed and immersed for 2 days into a corrosive medium consisting of a M/10 (10 moles per liter sulfuric acid solution). The weight loss of the strip amounts to 148 mg./dm.^{2}/day.

Example XV

Example XIV is repeated with the same corrosive liquid to which are added 10 p.p. m. of ethoxystearylimidazoline (manufactured by Doittau, Produits Chimiques, Corbeil,

France), and sulfur in various amounts in the form of a 1% solution in carbon disulfide, to form in the corrosive liquid a colloidal suspension of the latter.

The weight losses of the strips, corresponding to different amounts of sulfur in the liquid are given in Table VIII.

TABLE VIII

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	31
3	3.5
10	3.3
30	3.3
100	3.6
1,000	19.0

Example XVI

Example XIV is repeated with a corrosive liquid, consisting of a 1 M sulfuric acid solution. The weight loss of the strip amounts to 476 mg./dm.²/day.

Example XVII

Example XV is repeated with a corrosive liquid as used in Example XVI to which there are added 30 p.p.m. of ethoxystearylimidazoline and various amounts of sulfur in the form of a 1% solution in carbon disulfide.

The weight losses of the strips are given in Table IX.

TABLE IX

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	34.8
3	5.0
10	5.2
30	3.4
100	6.0
1,000	20.2

Example XVIII

Example XIV is repeated with a corrosive liquid consisting of a 10 M sulfuric acid solution. The weight loss of the strip amounts to 930 mg./dm.²/day.

Example XIX

Example XV is repeated with a corrosive liquid as used in Example XVIII to which there are added 100 p.p.m. of ethoxystearylimidazoline and various amounts of sulfulr in the form of a 1% solution in carbon disulfide.

The weight losses of the strips are given in Table X.

TABLE X

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	317
3	4.0
10	3.6
30	4.5
100	4.3
1,000	9.5

Example XX

A soft steel strip as annealed and cooled down in Example XIV is immersed for 4 days into a corrosive medium consisting of a M/10 acetic acid solution. The weight loss of the strip amounts to 23.2 mg./dm.²/day.

Example XXI

Example XX is repeated with the same corrosive liquid to which there are added 10 p.p.m. of N-tallow propylenediamine dioleate, manufactured by Armour and Co., and various amounts of sulfur in the form of a 0.2% solution in ethyl alcohol, to form in the corrosive liquid a colloidal suspension of the latter.

The weight losses of the strips, corresponding to different amounts of sulfur in the liquid are given in Table XI.

TABLE XI

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	25.4
3	17.0
10	16.7
30	16.9
100	16.8
1,000	24.9

Example XXII

Example XX is repeated with a corrosive liquid consisting of a 1 M acetic acid solution. The weight loss of the strip amounts to 32.4 mg./dm.²/day.

Example XXIII

Example XXI is repeated with a corrosive liquid as used in Example XXII to which there are added 30 p.p.m. of N-tallow propylenediamine dioleate and various amounts of sulfur in the form of a 0.2% solution in ethyl alcohol.

The weight losses of the strips are given in Table XII.

TABLE XII

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	26.5
3	12.4
10	12.7
30	17.0
100	21.0
1,000	27.4

Example XXIV

Example XX is repeated with a corrosive liquid consisting of a 10 M acetic acid solution. The weight loss of the strip amounts to 126 mg./dm.²/day.

Example XXV

Example XXI is repeated with a corrosive liquid as used in Example XXIV to which there are added 100 p.p.m. of N-tallow propylenediamine dioleate and various amounts of sulfur in the form of a 0.2% solution in ethyl alcohol.

The weight losses of the strips are given in Table XIII.

TABLE XIII

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	92
3	32.6
10	33.4
30	32.0
100	40.0
1,000	54.0

Example XXVI

A soft steel strip as annealed and cooled down in Example XIV is immersed for one day into a corrosive medium consisting of a M/10 perchloric acid solution.

The weight loss of the strip amounts to 120 mg./dm.²/day.

Example XXVII

Example XXVI is repeated with the same corrosive liquid to which there are added 100 p.p.m. of hexamethylenetetramine and various amounts of sulfur in the form of a 0.6% solution in cyclohexanone, to form in the corrosive liquid a colloidal suspension of the latter.

The weight losses of the strips, corresponding to different amounts of sulfur in the liquid, are given in Table XIV.

TABLE XIV

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	32.7
3	5.1
10	4.7
30	5.3
100	9.7
500	42.8

Example XXVIII

Example XXVI is repeated with a corrosive liquid consisting of a 1 M perchloric acid solution.

The weight loss of the strip amounts to 282 mg./dm.²/day.

Example XXIX

Example XXVII is repeated with a corrosive liquid as used in Example XXVIII to which there are added 200 p.p.m. of hexamethylenetetramine and various amounts of sulfur in the form of a 0.6% solution in cyclohexanone.

The weight losses of the strips are given in Table XV.

TABLE XV

Concentration of S in p.p.m.	Weight loss in mg./dm.²/day
0	87
3	16.1
10	14.5
30	14.4
100	15.6
1,000	53.3

While the sulfur in the preceding examples has been introduced into the acidic solution in the form of a suspension or colloidal emulsion and in such a manner that the flocculation of the sulfur particles on the metallic surface is facilitated by avoiding that the electric charges of the particles prevent the sulfur atoms from becoming fixed, probably by adsorption, on the metal surface it should be mentioned that any other suitable method of fixing the sulfur atoms on the metal surface would be equally satisfactory. Thus, for example, the fixation of sulfur on the metallic surface could be effected equally well by bringing the metal surface to be protected into contact, prior to exposing the surface, to contact with the acidic corrosive medium containing said anti-corrosive agent, with a solution of elementary sulfur in an organic solvent or by using instead of elementary sulfur organic or inorganic compounds such as alkali metal polysulphides capable of setting free elementary sulfur under such conditions of use that the electrical charge of the produced sulfur particles does not prevent the fixation, probably by adsorption, of the sulfur atoms on the metal surface.

It will be understood that this invention is susceptible to further modification and, accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. A method of protecting iron and steel surfaces against electrochemical corrosion in an acidic aqueous medium having a corrosion of the acidic type on said metal surfaces and against the penetration of hydrogen developed in such media, comprising the steps of adding to the acidic aqueous medium a known anti-corrosive agent selected from the group consisting of long chain aliphatic fatty acids having at least 8 carbon atoms per molecule, aliphatic amines, quaternary ammonium salts of the aforesaid amines, and having at least 8 carbon atoms per molecule, imidazolines and organic sulfides having the formula R—S—R′ wherein R and R′ are hydrocarbon radicals containing from 1 to 20 carbon atoms per radical, in corrosion-inhibiting amounts, and adding also to the acidic aqueous medium finely divided elementary sulfur.

2. A method as described in claim 1, characterized in that sulfur is added to the medium at a rate of less than 1000 parts per million by weight.

3. A method as described in claim 1, characterized in that sulfur is dissolved into the medium.

4. A method as described in claim 1, wherein the average particle size of the elementary sulfur in the medium is below 500 microns.

5. A method as described in claim 1, wherein the average particle size of the elementary sulfur in the medium is below 100 microns.

6. A method as described in claim 1, characterized in that a liquid solution of sulfur in an organic solvent is introduced into the acidic medium so as to produce elementary sulfur in a highly dispersed state in the acidic medium.

7. A method as described in claim 1, further comprising the step of bringing the metallic surface to be protected into contact with a liquid solution of sulfur in an organic solvent prior to exposing the surface to contact with said acidic medium containing said anti-corrosive agent.

8. In the method of preparing a substantially non-corrosive medium from an acidic aqueous medium having a corrosive action of the acidic type on soft-steel and iron surfaces, the steps, in combination, of adding to said medium tetradecylamine in corrosion-inhibiting amounts and also adding a solution of sulfur in a solvent selected from the group consisting of ethyl alcohol, benzene and gasoline in such amounts as to produce in the medium a concentration of elementary finely dispersed sulfur of less than 150 parts per million by weight; thereby enhancing the anti-corrosive effect of tetradecylamine considerably.

9. A method of protecting iron and steel surfaces against electrochemical corrosion in an acidic aqueous medium having a corrosive action of the acidic type on said metal surfaces and against the penetration of hydrogen developed in such media, comprising the steps of adding to said acidic medium a substance known as anti-corrosive agent in acidic media, in corrosion-inhibiting amounts, and adding also to the acidic medium finely distributed elementary sulfur.

10. A method of protecting iron and steel surfaces against electrochemical corrosion in an acidic aqueous medium having a corrosive action of the acidic type on said metal surfaces, and against the penetration of hydrogen developed in such media, which method comprises adding to the acidic aqueous medium a corrosion-inhibiting amount of an aliphatic amine and finely distributed elemental sulfur in a concentration of less than 1000 parts by weight of sulfur per million parts by weight of said acidic aqueous medium.

11. The method of claim 1, wherein the known anti-corrosive agent is tetradecylamine.

12. The method of claim 1, wherein the known anti-corrosive agent is ethoxystearylimidazoline.

13. The method of claim 1, wherein the known anti-corrosive agent is tallow propylenediaminedioleate.

14. The method of claim 1, wherein the known anti-corrosive agent is hexamethylenetetramine.

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