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MEANS OF INHIBITING THE CORROSIVE ACTION OF SULFAMIC ACID ON ZINC GALVANIZE

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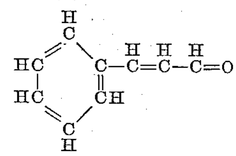
This invention relates to a means of reducing or inhibiting the corrosive action of sulfamic acid in contact with zinc. More specifically, the invention relates to the use of cinnamaldehyde, laurylaldehyde, and heptaldehyde to inhibit the rate of attack of sulfamic acid metal cleaners on zinc and particularly on zinc galvanized equipment.

Sulfamic acid is represented chemically by the formula HSO_3NH_2. It is a solid at room temperature and is a stable, relatively weak acid. It is used extensively as a metal cleaner for removing hard water scale, oxides, protein deposits and various stains from ferrous metals, copper, brass and similar metals, but is ordinarily too corrosive to be suitable for cleaning zinc or zinc galvanize. Even at room temperature sulfamic acid rapidly attacks zinc galvanize; in aqueous solution at concentrations as low as 1.5% by weight, it is capable of completely dissolving a zinc galvanize coating from a ferrous metal base in two to three hours. Repeated use of sulfamic acid even for short periods will severely corrode zinc galvanized equipment. The corrosive effect of the acid on zinc increases with temperature, and galvanize may be removed in less than 30 minutes at a temperature of 140° F.

Although sulfamic acid is widely used for cleaning other metals, there has been a need for a safe, effective rust, protein deposit and scale remover for use on galvanize, especially in the food industry for cleaning processing equipment. The desirability of a sulfamic type cleaner which may be used on zinc as well as on brass, copper and other surfaces, without corrosive effect, and which may be used on food procesing equipment without danger of contaminating food products, will be apparent.

This invention is predicated in part on the empirical determination and discovery that a small quantity of certain aldehydes, specifically cinnamaldehyde, laurylaldehyde and heptaldehyde, either alone or in combination, are highly effective to inhibit corrosion of zinc and zinc galvanize by sulfamic acid.

These aldehydes are depicted by the following chemical formulae,

cinnamaldehyde: 

laurylaldehyde: $CH_3(CH_2)_{10}-\overset{H}{C}=O$

heptaldehyde: $CH_3(CH_2)_5-\overset{H}{C}=O$

They are liquids at room temperature and are commercially available.

It is believed that when cinnamaldehyde, laurylaldehyde or heptaldehyde is added to sulfamic acid, the aldehyde and acid react to produce the aldehyde sulfamate and water:

$$R\overset{H}{C}=O + H-\underset{H}{N}-SO_3H \longrightarrow$$

$$R\overset{OH}{\underset{H}{C}}-\overset{H}{N}-SO_3H \longrightarrow R\overset{H}{C}=N-SO_3H + H_2O$$

where R designates the organic group. Apparently, in admixture with an excess of sulfamic acid, the aldehyde sulfamate inhibits or reduces the attack of zinc by the sulfamic acid. It is further theorized, although I do not wish to be limited in this regard, that this aldehyde sulfamate reacts with the zinc to form the zinc salt of the sulfate, which is deposited as a thin layer over the zinc surface and thereby protects the surface from corrosion by the acid.

In the practice of this invention, cinnamaldehyde, laurylaldehyde and/or heptaldehyde are added to sulfamic acid in the amount of about 0.5 to 5% by weight of the dry acid. These proportions are not especially critical, but are preferred for reasons to be explained. At present, about 2% of cinnamaldehyde is preferred for ordinary use.

As suggested, the quantity of aldehyde which is added to the acid is preferably not over a few percent. It is characteristic of these aldehydes that each possesses a strong odor, and if used in quantities larger than about 5% by weight of the dry acid, the resultant mixture has a strong (although not necessarily unpleasant) odor. Although larger proportions increase the inhibitory effect, aldehyde contents larger than 5% do not appear to produce commensurately better results, and become less economical.

The inhibiting effect of these compounds on the rate of attack of sulfamic acid on zinc is truly remarkable. For example, under comparable conditions, a composition comprising 2 parts by weight cinnamaldehyde added to 98 parts of sulfamic acid attacks zinc at a rate which is only about 3% the rate at which zinc is attacked by sulfamic acid alone. Heptaldehyde and laurylaldehyde are not quite as effective in inhibiting effect as cinnamaldehyde, although they are nonetheless of utility.

I have also discovered that the inhibiting effect of cinnamaldehyde, laurylaldehyde, and heptaldehyde on sulfamic acid is further augmented by admixing with the sulfamic acid and aldehyde one or more compounds selected from the class consisting of ethylenediaminetetraacetic acid (EDTA), cane sugar, wetting agents such as dodecyl benzene sulfonic acid or its sodium salt, quinine sulfate, quinine hydrochloride, zinc oxide, magnesium oxide, calcium sulfate, zinc sulfate and sodium sulfate. These compounds may be referred to as secondary inhibiting agent. The presence of a secondary inhibiting agent is not essential for the aldehyde to inhibit the attack of zinc by the acid, but the use of one or more of these materials surprisingly increases the inhibiting effect of the aldehyde on the acid, and is therefore preferred. Moreover, use of one or more secondary inhibiting agents makes possible the incorporation of a smaller amount of aldehyde to achieve a given inhibiting effect and at least in some instances lower cost of a secondary agent affords a commercial advantage.

When one or more of the aldehydes referred to are contacted with sulfamic acid, water is produced, as previously shown. The presence of water in sulfamic acid-aldehyde sulfamate mixture is undesirable for some purposes, for example, if the cleaner mixture is to be sold as a dry powder. Such moisture may be removed by the incorporation in the mixture of zinc oxide, magnesium oxide, anhydrous calcium sulfate, anhydrous zinc sulfate, or anhydrous sodium sulfate, which act as dessicants or anti-caking agents as well as increasing the inhibiting effect of the aldehyde. Alternately, undesirable moisture may be removed by mechanical methods, and the use of the anti-caking agents is not essential, although it is preferred.

The secondary inhibiting agents may be utilized in combination with about 0.5 to 5% (by weight of the final mixture) of one or more of the aldehydes, in the following approximate proportions:

	Percent
Cane sugar, zinc oxide or magnesium oxide	2 to 10
NA_2Ca, EDTA	0 to 3
Wetting agent	0 to 2
Anhydrous calcium sulfate, zinc sulfate or sodium sulfate	0 to 5
Anhydrous quinine sulfate or quinine hydrochloride	0 to 5
Sulfamic acid, balance to	100

The dry combination of aldehyde and sulfamic acid, and secondary inhibiting agents if any, may suitably be used on zinc galvanize in aqueous solution at a concentration of about 1 to 8 ounces of the dry mix per gallon, at temperatures from about 60° F. to about 140° F. The time of contact will vary with the quantity and type of scale, oxide or coating being removed.

It is also contemplated that an inhibitor concentrate may be produced for commercial sale, for addition by the purchaser to dry sulfamic acid prior to use of the acid in cleaning zinc. As an illustration of an inhibitor concentrate for use with sulfamic acid, mixtures of the following approximate compositions are effective:

Sulfamic acid	parts by weight	2 to 10
Cinnamaldehyde	parts	1 to 5
or		
Heptaldehyde	do	1 to 5
or		
Laurylaldehyde	do	1 to 5
Cane sugar	do	5 to 10
Na_2Ca, EDTA	do	1 to 3
Wetting agent	do	0 to 2

In these proportions, there is nearly complete reaction of the aldehyde and sulfamic acid to yield the aldehyde sulfamate. The sulfamate or inhibitor concentrate is added to dry sulfamic acid at the rate of about 10 to 30 parts inhibitor concentrate to 70 to 90 parts acid. The resulting inhibited acid mixture may be used in about 1 to 8% aqueous solution. Alternately, the inhibitor concentrate mix may also be added directly to an aqueous solution of sulfamic acid with effective results. Under the latter circumstances, the inhibitor concentrate may suitably be added at a rate of about 0.2 ounces per gallon of a 1.8 ounce per gallon solution of sulfamic acid.

Tables I and II illustrate the inhibiting effect, in terms of weight of galvanize removed from unit area in unit time, of various combinations of cinnamaldehyde, heptaldehyde, laurylaldehyde and/or secondary inhibiting agents, with sulfamic acid, in comparison to the corresponding rate of attack of sulfamic acid alone.

TABLE I

Test No.	1	2	3	4	5	6	7	8	9	10
Sulfamic Acid, percent	100	98	98	98	89.75	89.75	94.75	92.75	99	95
Cinnamaldehyde, percent		2								
Heptaldehyde, percent			2					2		
Laurylaldehyde, percent				2						
$2CaSO_4.H_2O$, percent					5		5	5		
$ZnSO_4.H_2O$, percent						5				
ZnO, percent					5	5				
Wetting Agent, percent					0.25	0.25	0.25	0.25	1.0	
Quinine Sulfate, percent										5.0
Oz./Gallon Conc	8	8	4	4	8	8	8	8	8	8
Metal removed, mg./dm.^{2}/hour	1,185	32	134	284	774	283	493	238	265	589

TABLE II

Test No.	11	12	13	14	15	16	17	18
Sulfamic Acid, percent	100	92.5	88.0	87.0	89.5	90.0	90.5	90.5
Cinnamaldehyde, percent			2.0	2.0	2.0	2.0	2.0	2.0
$2CaSO_4{\cdot}H_2O$, percent			2.0	5.0		2.0	2.0	2.0
$ZnSO_4{\cdot}H_2O$, percent			2.0		3.0	5.0	5.0	5.0
ZnO, percent			5.0		5.0			
Cane Sugar, percent				5.0				
EDTA Na_2Ca, percent				1.0				
Wetting Agent, percent			1.0		0.5	1.0		
Quinine Sulfate, percent							0.5	
Quinine Hydrochloride, percent								0.5
Commercial Inhibitor, percent		7.5						
Metal removed, 2 oz./gallon/conc.,/mg./dm.^{2}/hour	51.7	5.4	6.5	8.2	8.3	16.0		3.0
Metal removed, 8 oz./gallon/conc.,/mg./dm.^{2}/hour	1,185	20.1	10.2	9.2	17.0	18.9	8.1	5.2

In these tables, the results are expressed in terms of milligrams of metal removed per square decimeter of metal area per hour of contact with the acid (mg./dm.^{2}/hour). All tests were conducted on uniform galvanized test strips for a period of three hours at a temperature of 70° F., at specified aqueous concentrations. It should be added that the rate of attack is most rapid when the acid first contacts the metal and that thereafer the rate slows considerably with time; the rates specified are the average quantity of metal dissolved per hour over the three-hour test period.

Test No. 1 in Table I shows that a solution of 8 ounces of sulfamic acid per gallon of water removed metal from a galvanized test strip at a rate of 1185 mg./dm.^{2}/hour. In sharp contrast to this, a combination of 2% cinnamaldehyde with 98% sulfamic acid under corresponding test conditions attacked galvanize at a rate of only 32 mg./dm.^{2}/hour. Tests 3 and 4 show that at concentrations of 4 ounces per gallon, 2% heptaldehyde and 2% laurylaldehyde respectively with 98% sulfamic acid were not as effective as cinnamaldehyde, but nonetheless were markedly better than sulfamic acid alone.

The tables show that although the secondary inhibiting agents of themselves effect a reduction in the rate of metal loss when used with sulfamic acid in the absence of the aldehydes, in general considerably better results are obtained when the secondary additives are used with the aldehydes. Thus, for example, as shown by comprising tests 2 and 14, 2% cinnamaldehyde and 98% sulfamic acid in aqueous solution attacked the test strip at a rate of 32 mg./dm.^{2}/hour, while a combination comprising 2% cinnamaldehyde, 5.0% $CaSO_4$ anhydrate, 5.0% cane sugar, 1.0% Na_2Ca EDTA, and the balance sulfamic acid, attacked the test strip at a rate of only 9.2 mg./dm.^{2}/hour under corresponding test conditions.

These general results may also be compared with the results achieved by a different type of commercially available product for inhibiting the corrosion of zinc by sulfamic acid, known as "Rhodine 140," which, combined with sulfamic acid in the recommended proportions of 7.5%, removed metal at a rate of 20.1 mg./dm.^{2}/hour.

In view of economy, ease of manufacturing, bulking, shipping and use, a preferred mixture in accordance with this invention is of the following composition:

	Percent
Sulfamic acid	87.0
Cinnamaldehyde	2.0
Cane sugar	5.0
Na_2Ca EDTA	1.0
Calcium sulfate anhydrate	5.0

This mix is preferably used at the rate of 1 to 8 ounces per gallon water at a temperature in the range of about 60 to 140° F. on zinc galvanize. Generally speaking, the higher the temperature or the longer the metal is in contact with the solution, the greater the corrosion of the galvanize will be. The optimum concentration of the solution, the time and the temperature utilized for cleaning the metal, will depend largely on the quantity and nature of the deposit which is to be removed. However, in normal cleaning operations, 2 to 4 ounces of mix per gallon at 60 to 80° F. are adequate to remove a deposit in 5 to 20 minutes.

While I have described herein the preferred embodiment of my invention, the invention also includes other embodiments coming within the scope of the appended claims.

What is claimed is:

1. A dry mixture, adapted for cleaning of zinc galvanize upon dissolution in water, and consisting essentially of (a) from about 0.5 to about 5.0 percent by weight, based on the total weight, of cinnamaldehyde; (b) from about 2.0 to about 9.0 percent by weight, based on the total weight, of a desiccant selected from the group consisting of zinc oxide, magnesium oxide, anhydrous calcium sulfate, anhydrous zinc sulfate, anyhdrous sodium sulfate, calcium sulfate monohydrate, zinc sulfate monohydrate, and mixture thereof; and (c) from about 86.0 to about 97.5 percent by weight, based on the total weight, of sulfamic acid.

2. A dry mixture as defined in claim 1 also including about 0.5 to about 5.0 percent by weight, based on the total weight, of a quinine salt selected from the group consisting of quinine sulfate, quinine hydrochloride, and mixtures thereof.

3. A dry mixture as defined in claim 1 also including about 0.25 to about 1.0 percent by weight, based on the total weight, of a wetting agent selected from the group consisting of dodecyl benzene sulfonic acid and its sodium salt.

4. A dry mixture as defined in claim 1 also including 0 to about 3 percent by weight, based on the total weight, of the disodium monocalcium salt of ethylenediamine tetra-acetic acid and about 2 to about 10 percent by weight, based on the total weight, of cane sugar.

5. A dry mixture, adapted for cleaning of zinc galvanize upon dissolution in water, and consisting essentially of about 87.0 percent by weight sulfamic acid, about 2.0 percent by weight cinnamaldehyde, about 5.0 percent

by weight calcium sulfate monohydrate, about 5.0 percent by weight cane sugar and about 1.0 percent by weight of the disodium monocalcium salt of ethylenediamine tetra-acetic acid.

6. A dry mixture, adapted for cleaning of zinc galvanize upon dissolution in water, and consisting essentially of about 90.5 percent by weight sulfamic acid, about 2.0 percent by weight cinnamaldehyde, about 2.0 percent by weight calcium sulfate monohydrate, about 5.0 percent by weight zinc sulfate monohydrate, and about 0.5 percent by weight of a quinine salt selected from the group consisting of quinine sulfate, quinine hydrochloride, and mixtures thereof.

7. The method of inhibiting the attack of sulfamic acid on a zinc galvanize surface which comprises treating said surface with an aqueous solution of a dry mix consisting essentially of (a) from about 0.5 to about 5.0 percent by weight, based on the total weight of cinnamaldehyde; (b) from about 2.0 to about 9.0 percent by weight, based on the total weight, of a desiccant selected from the group consisting of zinc oxide, magnesium oxide, anhydrous calcium sulfate, anhydrous zinc sulfate, anhydrous sodium sulfate, calcium sulfate monohydrate, zinc sulfate monohydrate and mixtures thereof; and (c) from about 86.0 to about 97.5 percent by weight based on the total weight, of sulfamic acid; said aqueous solution containing from about 2 to about 8 ounces per gallon of said dry mix.

8. The method of inhibiting the attack of sulfamic acid on a zinc galvanize surface which comprises treating said surface with an aqueous solution of a dry mix consisting essentially of about 87.0 percent by weight sulfamic acid, about 2.0 percent by weight cinnamaldehyde, about 5.0 percent by weight calcium sulfate monohydrate, about 5.0 percent by weight cane sugar, and about 1.0 percent by weight of the disodium monocalcium salt of ethylenediamine tetra-acetic acid; said aqueous solution containing from about 2 to about 8 ounces per gallon of said dry mix.

9. The method of inhibiting the attack of sulfamic acid on a zinc galvanize surface which comprises treating said surface with an aqueous solution of a dry mix consisting essentially of about 90.5 percent by weight sulfamic acid, about 2.0 percent by weight cinnamaldehyde, about 2.0 percent by weight calcium sulfate monohydrate, about 5.0 percent by weight zinc sulfate monohydrate, and about 0.5 percent by weight of a quinine salt selected from the group consisting of quinine sulfate, quinine hydrochloride, and mixtures thereof; said aqueous solution containing from about 2 to about 8 ounces per gallon of said dry mix.

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