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## ACID INHIBITING AGENT

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This invention relates to the inhibition of the solvent action of hydrogen evolving acids upon metals while permitting the acid to act upon the corrosion products of the metals or foreign depositions, thereby effecting the removal of such corrosion products and depositions from a metallic surface with the minimum loss of valuable free metal and the minimum consumption of acid. More particularly, the invention relates to a novel class of inhibitors for use in pickling and cleaning acids and to the product formed by the addition of one or more members of that class to such acids.

It is known that a large variety of substances have been used as inhibitors in acid pickling baths and acid cleaning solutions such as the acid extract of coal, sludges from the sulfuric acid treatment of coal tar or petroleum, mouldy flour, glue, diorthotolyl thiourea, cellulose pulp waste, thiocyanates, thiobenzamide, quinoline and its derivatives, acridine and its derivatives and thiazoles. Various disadvantages are connected with the use of such substances as inhibitors. For example, some of the substances show a low efficiency, are non-available and expensive to make, are water insoluble, and are unstable in the acid used, particularly in more concentrated solutions of acid. Moreover, even some of the best pickling acid inhibitors heretofore in use have been low fusing resinous compounds which are apt to produce deposits on the metal causing spotting or streaking that interferes with subsequent treatment thereof, for instance, in galvanizing.

This invention has as one of its objects the preparation of a cleaning or pickling acid solution containing an inhibitor which has a relatively high fusion point and is non-resinous in character. A further object is the preparation of an acid inhibitor that is water soluble. A still further object is the preparation of a concentrated acid solution containing an inhibitor of the above described character, which solution can be shipped as such and requires no treatment other than dilution for adaptation to a given pickling process. Another object is the preparation of an inhibited pickling solution in which the inhibitor has a high efficiency. Other objects and advantages of the invention will be apparent by reference to the following description thereof.

These objects are accomplished by dispersing as an inhibitor in acid pickling solutions the product obtained by condensing an amine and sulfonated aromatic amine with an aldehyde which process is preferably followed by further condensation with carbon bisulfide. For example, aniline and sulfanilic acid are condensed with acetaldyhyde and the resulting product used as an inhibitor or further condensed with carbon bisulfide and used as an inhibitor. In either case, a water soluble material with a fusion point well above 150° C. is obtained and the product is better adapted to certain inhibitor work than water insoluble, low fusing, resinous compounds. Generally speaking, we have found that the product obtainable by chemically combining an amine, an aldehyde, a sulfonated aromatic amine and carbon bisulfide is more highly efficient as an acid inhibitor than the amine-aldehyde-sulfonated aromatic amine product.

As a preferred embodiment of our invention, we add suitable amounts of the high fusing, water-soluble inhibitors herein described to concentrated commercial acids, thereby producing stock pickling solutions which can be shipped as such without destruction of the inhibitor and need no further attention other than dilution to the proper strength for use in the pickling bath.

While our invention is susceptible of considerable variation in the manner of its practical application, the following examples will illustrate some of the products falling within the invention and how they may be prepared. The proportions given are in parts by weight.

### *Example 1*

One hundred and eighty-six parts of aniline is mixed with the aqueous solution formed by adding 382 parts of sulfanilic acid to 1000 parts of water containing 80 parts of sodium hydroxide. The aniline-sodium sulfanilate mixture is added slowly through a condenser to 200 parts of acetalydehyde in a kettle equipped with a jacket, a coil for heating and cooling, and an agitator. The temperature is kept below 30° C. during the addition of the aniline-sodium sulfanilate mixture and raised to 50–60° C. for one hour after the entire mixture is added.

At this point either of two steps is followed. (1) The reaction mass is evaporated to dryness by direct heating at atmospheric pressure. The solid product is found to be a good acid inhibitor. (2) The reaction mass is cooled to 30° C. and 228 parts of carbon bisulfide then added through the condenser. The temperature is raised to 50–60° C. and held at this point for three hours, allowing the carbon bisulfide to reflux. At the end of this time the unreacted carbon bisulfide is drawn off under vacuum and the charge evaporated to dryness by direct heating at atmospheric pressure. The red-amber solid product, when added to a pickling acid, is found to be an excellent acid inhibitor.

### *Example 2*

To 191 parts of metanilic acid dissolved in 500 parts of water containing 40 parts of sodium hydroxide are added to 93 parts of aniline and the mixture added slowly through a condenser into 100 parts of acetaldehyde in a kettle as used in Example 1. The aldehyde is condensed simultaneously with the aniline and sodium metanilate by heating one hour at 50–60° C. The resulting

aqueous solution is evaporated to dryness to obtain a dry water soluble solid which is found to have good inhibiting properties or it is further condensed with 228 parts of carbon bisulfide. This carbon bisulfide condensation is carried out at 50–60° C. for three hours. After removal of unreacted carbon bisulfide the remaining aqueous solution is evaporated to dryness and the solid obtained is found to be an excellent acid inhibitor.

*Example 3*

A mixture of 303 parts of 2-naphthylamine-5:8-disulfonic acid in 1000 parts of water containing 80 parts of sodium hydroxide and 93 parts parts of aniline is reacted with 100 parts of acetaldehyde and condensed with 228 parts of carbon bisulfide. When freed from unreacted carbon bisulfide the aqueous solution is evaporated to a dry solid which has high inhibiting value in acid pickling baths.

*Example 4*

One hundred and seven parts of o-toluidine are mixed with 191 parts of sulfanilic acid dissolved in 500 parts of water containing 40 parts of sodium hydroxide and the mixture reacted with 100 parts of acetaldehyde. When the resultant solution is evaporated to dryness a solid condensation product with good inhibiting value is obtained. The solution obtained from the o-toluidine-sodium sulfanilate-aldehyde reaction may be treated with 228 parts of carbon bisulfide to bring about a further condensation. The excess carbon bisulfide is removed under vacuum and the solid product obtained by evaporation is found to possess high inhibiting value.

*Example 5*

One hundred and twenty-one parts of xylidine are used in place of the o-toluidine in the procedure given in Example 4 and there are obtained solid products that may be dispersed as inhibitors in pickling solutions.

*Example 6*

Ninety-three parts of aniline are mixed with 191 parts of sulfanilic acid dissolved in 500 parts of water containing 40 parts of sodium hydroxide and the mixture slowly added through a condenser to 228 parts of heptaldehyde in a kettle as used in Example 1. The temperature is slowly raised to 100° C. and held there for one hour. The reaction mass is cooled to 30° C. and 228 parts of carbon bisulfide are then added through the condenser. The temperature is raised to the reflux point, 50–60° C., and held for three hours. The unreacted carbon bisulfide is drawn off by vacuum and the charge evaporated to dryness. The product is very effective as an acid inhibitor.

*Example 7*

A mixture of 93 parts of aniline and 191 parts of sulfanilic acid dissolved in 500 parts of water containing 40 parts of sodium hydroxide is condensed with 140 parts of crotonaldehyde and the resulting product reacted under reflux with 228 parts of carbon bisulfide. The final solid product obtained on evaporation is found to be an excellent acid inhibitor.

In Examples 3, 6 and 7 it will be understood that the intermediate products obtained by condensation of the aldehyde, amine, and sulfonated aromatic amine, but before condensation with the carbon bisulfide, may be recovered in a suitable manner and employed as acid inhibitors.

As previously indicated, these examples are given merely to illustrate the new class of products which may be used as acid inhibitors and are not intended to limit the scope of the invention. In general, we may effect the condensation with any primary or secondary aliphatic or aromatic amine, and sulfonated aromatic amine, and any aliphatic or aromatic aldehyde.

Good results are obtainable when the condensations are effected with the following (1) amines: aniline, o-toluidine, p-toluidine, xylidines, alpha-naphthylamine, ethanol amines, butyl amine, allyl amine, diethyl amine, dibutyl amine, diphenyl amine, dibenzyl amine, phenyl-α-naphthylamine, phenyl-β-naphthylamine, ditolyl amine, a-a'-dinaphthylamine, p-phenylene diamine, meta-toluylene diamine, benzidine, tolidine, piperidine, dianisidine, methyl or ethyl aniline; (2) aldehydes: acetaldehyde, heptaldehyde, crotonaldehyde, butyraldehyde, formaldehyde, furfuraldehyde, or benzaldehyde; and (3) sulfonated aromatic amines: sulfanilic acid, metanilic acid, 2-naphthylamine-5:8-disulfonic acid, sulfonated toluidines, sulfonated xylidines, mono- and di-sulfonated naphthylamines. It will be understood, of course that the various amines, sulfonated aromatic amines and aldehydes may be condensed and the product employed as an acid inhibitor but it is preferable to include carbon bisulfide in the condensation whereby a superior inhibitor is formed.

While the condensation reactions may be effected with any one of the obviously large number of combinations of amine, sulfonated aromatic amine, aldehydes, and carbon bisulfide, our preferred combinations are: aniline, sulfanilic acid. acetaldehyde, carbon bisulfide, aniline, metanilic acid, acetaldehyde, carbon bisulfide; o-toluidine, sulfanilic acid, acetaldehyde, carbon bisulfide.

Different ratios of aldehyde, amine, and carbon bisulfide may be found preferable with different amines, sulfonated amines and aldehydes. The invention is not necessarily restricted to those specific ratios given in the examples. In general, however, it is preferable to use the constituents for the condensation in the following ratios: for every mole of amine between 0.5 and 5 moles of sulfonated aromatic amine, between 1.5 and 6 moles of aldehyde, and between 1 and 3 moles of carbon disulfide. Naturally, the invention contemplates the use of greater or less proportions of the reactants than those above given but so far the proportions within the above preferred range have been found to be most advantageous.

It is possible to vary the order of addition of the amine and sulfonated amine to aldehyde and carbon bisulfide. Thus, the carbon bisulfide and aldehyde may be reacted together first and as a second stage the amine and sulfonated amine mixture may be added to the aldehyde-carbon bisulfide condensation product. On the other hand, the carbon bisulfide may be added to the amine and the reaction product formed thereby may be mixed with the aqueous solution of sulfonated amine prior to the addition of the aldehyde. In practicing the invention, however, it is essential that the amine and sulfonated aromatic amine be employed as such. We have found it decidedly undesirable to form the sulfonated amine in the reaction product by sulfonating an aldehyde-amine condensation product because of the difficulty involved in controlling the sulfonation.

The temperature at which the reactions are carried out will vary with the constituents used, and the time of heating for the condensation reactions can vary within rather wide limits. Obviously, the temperature employed should not exceed the decomposition point of the various reactants. Generally from 3 to 9 hours heating before evaporating to dryness are sufficient to give the desired products.

When any one of the class of products described herein is added to a pickling acid, such as hydrochloric or sulfuric acid, diluted to a strength suitable for the acid treatment of metals to remove corrosion products or extraneous scale deposits, an effective inhibition with respect to the action of the acid on the free metal results if a small quantity of the inhibitor has been added, say from 0.01 to 1 part by weight of inhibitor to 100 parts of acid.

Table I sets forth as examples some of the tests conducted to measure the inhibiting efficiencies in the treatment of metals. In each of these tests a piece of annealed mild steel tubing ½" in diameter and 1¼" long was immersed in 5% sulfuric acid maintained at a temperature of 82° C. Beginning ten minutes after immersing the metal the volume of hydrogen evolved during one hour was collected and measured from the pickling bath containing no inhibitor and from baths containing 0.01% of the various new inhibitors. The metal subjected to the action of the free acid displaced 800 cc. of hydrogen per hour while in the presence of an inhibitor only small amounts of hydrogen were evolved. For example, in the presence of Inhibitor No. II only about 4 cc. of hydrogen per hour was displaced, so that an inhibition of 99.5% was obtained.

*Table I*

| Inhibitor number | Materials used | Moles | Percent inhibition |
|---|---|---|---|
| I | Sulfanilic acid | 1 | |
| | Aniline | 1 | |
| | Acetaldehyde | 2 | |
| | Carbon bisulfide | 3 | 99.8 |
| II | Metanilic acid | 1 | |
| | Aniline | 1 | |
| | Acetaldehyde | 2 | |
| | Carbon bisulfide | 3 | 99.5 |
| III | 2-Naphthylamine-5:8-disulfonic acid | 1 | |
| | Aniline | 1 | |
| | Acetaldehyde | 3 | |
| | Carbon bisulfide | 3 | 97.4 |
| IV | Sulfanilic acid | 1 | |
| | o-Toluidine | 1 | |
| | Acetaldehyde | 2 | |
| | Carbon bisulfide | 3 | 97.9 |
| V | Sulfanilic acid | 1 | |
| | Xylidine | 1 | |
| | Acetaldehyde | 2 | |
| | Carbon bisulfide | 3 | 99.5 |
| VI | Sulfanilic acid | 1 | |
| | Aniline | 1 | |
| | Heptaldehyde | 2 | |
| | Carbon bisulfide | 3 | 90.7 |
| VII | Sulfanilic acid | 1 | |
| | Aniline | 1 | |
| | Crotonaldehyde | 2 | |
| | Carbon bisulfide | 3 | 99.4 |

It will be understood that the inhibiting action of the compounds we have described may vary within relatively wide limits, depending upon the concentration of the inhibitor, the strength and kind of acid employed, and the temperature of the acid solution.

In general, the inhibiting agents produced in accordance with our invention are found to possess excellent properties as inhibitors against the unnecessary and wasteful action of strong mineral, pickling and cleaning acids of the hydrochloric and sulfuric acid type on the free metal following and during oxide film and scale removal. By their use, large economies in acid consumption are realized. Furthermore, the atmosphere of the pickling room is kept free from the obnoxious acid fumes created by the escaping hydrogen. In addition, the inhibitors of this particular class are relatively high fusing solids, nonresinous in character, and by their use the deposition of undispersed gummy particles on the surface of the clean metal is avoided. These deposits of certain other low-fusing, resinous inhibiting agents often cause considerable trouble in subsequent working of the metal and in zinc coating processes. Furthermore, most of the members of this new class of inhibitors are water soluble which gives them an advantage over the water insoluble type of inhibitor.

Another feature of the inhibitors of the class described in this invention is their stability in concentrated pickling baths and in concentrated pickling acid prior to dilution. Heretofore, because of the instability of acid inhibitors in concentrated pickling acids, it has been customary to add the inhibitor to the diluted pickling bath. This involves separate handling of the acid and the inhibitor by the user and the trouble of mixing them together homogeneously. As previously indicated, according to our invention, we may avoid these disadvantages by adding the inhibitor directly to a concentrated pickling acid in the plant and thereafter shipping the product as such to the consumer who may store it for later use or dilute it directly to the proper strength for his particular pickling process. Concentrated stock solutions of this character may be stored for some time without deterioration or diminution of the inhibiting qualities thereof.

In our description of the present invention, we have used the terms pickling acid and concentrated pickling acid. We wish it to be understood that by pickling acids we mean non-oxidizing acids, and more specifically, non-oxidizing mineral acids, such as, for example, sulfuric acid, hydrochloric acid and their equivalents. By concentrated pickling acid, we mean non-oxidizing acids of the class above described having concentrations normally employed commercially such as, for example, in the case of sulfuric acid, acid having a specific gravity in the range of about 60–66 degrees Bé.: that is, about 75–93% $H_2SO_4$ by weight. With respect to hydrochloric acid, we designate a concentrated acid as one having a specific gravity of about 18–22 degrees Bé., that is to say, a percentage composition of about 28–35% HCl by weight.

It will be understood that our invention is not limited to the tank method of pickling metals. Acid solutions containing our inhibitors may be employed in cleaning pipe systems, and, in general, to remove the corrosion products, oxidation products, scale, etc., from the surface of a metal, particularly when the material is being prepared for some kind of protective coating.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or description except as indicated in the following claims.

We claim:

1. The product obtainable by simultaneously reacting a sulfonated aromatic amine of the group

consisting of primary and secondary amines and an amine of the group consisting of primary and secondary aliphatic and aromatic amines with an aldehyde in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of the amine.

2. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and a primary aromatic amine with an aldehyde in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of the amine.

3. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and an amine of the group consisting of primary and secondary aromatic amines with an aliphatic aldehyde in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of the amine.

4. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and a primary aromatic amine with acetaldehyde in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of the amine.

5. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and aniline with acetaldehyde in proportions corresponding to about 1.5 to about 6.0 moles of acetaldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of aniline.

6. The product obtainable by simultaneously reacting sulfanilic acid and aniline with acetaldehyde in proportions corresponding to about 1.5 to about 6.0 moles of acetaldehyde and about 0.5 to about 5.0 moles of the sulfonated amine to each mole of aniline.

7. The product obtainable by simultaneously reacting sulfanilic acid and aniline with acetaldehyde in proportions corresponding to about one mole of sulfanilic acid and about two moles of acetaldehyde to each mole of aniline.

8. The product obtainable by simultaneously reacting a sulfonated aromatic amine and an amine of the group consisting of primary and secondary aliphatic and aromatic amines with an aldehyde and then condensing with carbon disulfide.

9. The product obtainable by simultaneously reacting a sulfonated aromatic amine and an amine of the group consisting of primary and secondary aliphatic and aromatic amines with an aldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

10. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and an amine of the group consisting of primary and secondary aliphatic and aromatic amines with an aldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

11. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and an amine of the group consisting of primary and secondary aromatic amines with an aliphatic aldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

12. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and a primary aromatic amine with an aliphatic aldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

13. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and an amine of the group consisting of primary and secondary aliphatic and aromatic amines with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

14. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and a primary aromatic amine with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the aldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of amine.

15. The product obtainable by simultaneously reacting a sulfonated primary aromatic amine and aniline with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of acetaldehyde, about 0.5 to about 5.0 moles of the sulfonated amine and about 1 to about 3 moles of carbon disulfide to each mole of aniline.

16. The product obtainable by simultaneously reacting sulfanilic acid and aniline with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about one mole of sulfanilic acid, about two moles of acetaldehyde and about 3 moles of carbon disulfide per mole of aniline.

17. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product of claim 1.

18. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product of claim 7.

19. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product of claim 8.

20. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product of claim 9.

21. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product of claim 16.

22. The method of cleaning or pickling metals which comprises subjecting the same to the action of a non-oxidizing mineral acid pickling solution having dispersed therein a small amount of the product defined in claim 8.

23. The method of cleaning or pickling metals which comprises subjecting the same to the action of a non-oxidizing mineral acid pickling

solution having dispersed therein a small amount of the product defined in claim 9.

24. The method of cleaning or pickling metals which comprises subjecting the same to the action of a non-oxidizing mineral acid pickling solution having dispersed therein a small amount of the product defined in claim 16.

25. The product obtainable by simultaneously reacting an unsubstituted naphthylamine sulfonic acid and unsubstituted toluidines with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the naphthylamine sulfonic acid and about 1 to about 3 moles of carbon disulfide to each mole of toluidine.

26. The product obtainable by simultaneously reacting unsubstituted toluidine sulfonic acids and an unsubstituted naphthylamine with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the toluidine sulfonic acids and about 1 to about 3 moles of carbon disulfide to each mole of naphthylamine.

27. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product obtainable by simultaneously reacting an unsubstituted naphthylamine sulfonic acid and unsubstituted toluidines with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the naphthylamine sulfonic acid and about 1 to about 3 moles of carbon disulphide to each mole of toluidine.

28. A pickling acid solution for cleaning or pickling metals which contains a small amount of the product obtainable by simultaneously reacting unsubstituted toluidine sulfonic acids and an unsubstituted naphthylamine with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the toluidine sulfonic acids and about 1 to about 3 moles of carbon disulfide to each mole of naphthylamine.

29. The method of cleaning or pickling metals which comprises subjecting the same to the action of a non-oxidizing mineral acid pickling solution having dispersed therein a small amount of the product obtainable by simultaneously reacting an unsubstituted naphthylamine sulfonic acid and unsubstituted toluidines with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the naphthylamine sulfonic acid and about 1 to about 3 moles of carbon disulfide to each mole of toluidine.

30. The method of cleaning or pickling metals which comprises subjecting the same to the action of a non-oxidizing mineral acid pickling solution having dispersed therein a small amount of the product obtainable by simultaneously reacting unsubstituted toluidine sulfonic acids and an unsubstituted naphthyamine with acetaldehyde and then condensing with carbon disulfide in proportions corresponding to about 1.5 to about 6.0 moles of the acetaldehyde, about 0.5 to about 5.0 moles of the toluidine sulfonic acids and about 1 to about 3 moles of carbon disulfide to each mole of naphthylamine.

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