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CHEMICAL TREATMENT OF WELLS FOR THE PREVENTION OF CORROSION

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This invention relates to the chemical treatment of wells for the prevention of corrosion and, more particularly, it relates to inhibiting corrosive attack on metal equipment by well fluids containing water and sulfides and/or carbon dioxide.

Corrosion of oil field equipment is severe in areas where brines are produced with sour crudes. These corrosive brines generally contain sulfides, such as hydrogen sulfide, which are soluble in water and brines, and which cause the brines to become very corrosive to iron and steel. It has also been observed that those brines which contain corrosive sulfides frequently contain carbon dioxide which also exerts a corrosive effect. Furthermore, carbon dioxide itself has been observed to induce corrosion of metal equipment in gas and condensate wells and in deep oil wells, even where little or no sulfides are present.

It has recently been proposed to reduce the corrosiveness of sulfide containing brines by injecting into the producing well either continuously or batchwise small amounts of water soluble aldehydes, particularly formaldehyde. It has been stated that the formaldehyde apparently reacts slowly with a portion of the hydrogen sulfide in the presence of the brine to produce a thin protective film of a reaction product on the exposed metal surfaces. While the formaldehyde treatment described has been found to be beneficial in field practice, in many instances the use of formaldehyde is inefficient. For example, when formaldehyde is added to the well annulus between the tubing and casing, it immediately enters the fluid being produced through the tubing in large quantity, so that the presence of formaldehyde in the produced well fluids cannot be noted after a few hours. Field tests have shown that as high as 1500 parts per million of unreacted formaldehyde appear in the well effluent within 2 hours after adding several quarts to the well annulus. Furthermore, no formaldehyde can be found in the well fluid 10 hours after the treatment. The formaldehyde thus passes through the well equipment quickly and quite largely in an unreacted state. In those instances where the brines produced contain no sulfides and corrosion is due to carbon dioxide, formaldehyde is ineffective and does not inhibit corrosion.

It is an object of this invention, therefore, to provide an improved method for inhibiting corrosive attack on metal equipment by aqueous well fluids containing sulfides or carbon dioxide or mixtures thereof. It is a further object of this invention to improve the efficiency of treatment of oil wells for the purpose of inhibiting the corrosion induced by sulfide brines. Other objects will appear hereinafter.

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These objects are accomplished by the present invention, wherein the corrosive attack of metal equipment by aqueous well fluids containing sulfides, or carbon dioxide or mixtures thereof is substantially inhibited by adding to said well fluids a small amount, sufficient to retard said corrosive attack, of a preformed reaction product of an aqueous solution of formaldehyde with hydrogen sulfide.

I have found that the preformed reaction product of an aqueous solution of formaldehyde with hydrogen sulfide is an excellent inhibitor for retarding corrosion of metal equipment by sulfide brines, brines containing carbon dioxide and brines containing both sulfides and carbon dioxide. Such reaction product exhibits immediate effectiveness in inhibiting corrosion and is thus of particular advantage where the well fluids are being produced by pumping, because in pumping well practice the time of contact between the fluids being produced and the well equipment is at most only a few hours. As compared to formaldehyde, therefore, the inhibitor of my invention has the advantage of being immediately effective. It also gives greater protection against corrosion by sulfide brines than may be obtained by the use of formaldehyde itself, even when smaller amounts of the reaction product described herein are used. Furthermore, whereas formaldehyde is ineffective against carbon dioxide corrosion, the inhibitor of my invention effectively retards such corrosion.

The reaction of hydrogen sulfide with an aqueous solution of formaldehyde is strongly exothermic, and reaction occurs upon mere mixing of the reactants. The hydrogen sulfide reacts with the formaldehyde in varying proportions. When an amount of hydrogen sulfide is used which reacts with all of the formaldehyde present, i. e., when the aqueous solution of formaldehyde is completely saturated with hydrogen sulfide, there results an increase of weight, based on the anhydrous formaldehyde, of about 67 per cent. However, in accordance with my invention, the amount of hydrogen sulfide to be reacted may be considerably less than complete saturation, so that only an amount of hydrogen sulfide is reacted which results in an increase in weight of about 5 per cent, based on the anhydrous formaldehyde. Since the formaldehyde is reacted in aqueous solution, and since some commercial

aqueous formaldehyde solutions (formalin) usually contain about 37 per cent by weight of formaldehyde, the amount of hydrogen sulfide used when a 37 per cent aqueous formaldehyde solution is employed varies from about 2 to about 25 per cent by weight. Other concentrations of aqueous formaldehyde can be used, such as a 25 per cent by weight aqueous formaldehyde solution, the concentration of the formaldehyde not being critical. The formaldehyde solutions may contain other materials, such as methyl alcohol, for the purpose of preventing polymerization and freezing, as will be understood in the art.

The reaction products obtained vary from aqueous oily liquids to wax-like solids. All of such products have been found to be useful in my invention. Unreacted formaldehyde need not be separated from the reaction products obtained when an insufficient amount of hydrogen sulfide is used to react with all of the formaldehyde, but it may be separated if desired, such as by extracting the reaction products with ether.

The exact nature of the reaction products is unknown, but without being limited to any theory, it is believed that a mixture of sulfur-containing compounds, including mercaptans and possibly sulfides, is obtained. In this connection, it is interesting to note that the prior art has indicated that preformed mercaptans are ineffective as inhibitors of hydrogen sulfide corrosion when added to hydrogen sulfide brines. In view of the fact that the hydrogen sulfide-formaldehyde reaction products of my invention are very effective inhibitors of sulfide corrosion, it is obvious that such reaction products have not previously been employed for this purpose and that their action is quite specific and unpredictable.

As has been stated, the reaction of hydrogen sulfide with an aqueous solution of formaldehyde is strongly exothermic and occurs upon mere mixing of the reactants. Thus, when hydrogen sulfide in the amounts hereinabove stated is bubbled into an aqueous solution of formaldehyde at room temperature, the reaction taking place is rapid and the temperature approaches or may even exceed 100° F. Under these conditions, when the amount of hydrogen sulfide used is such as to saturate, that is, to completely react with all the formaldehyde present, the reaction product formed is a wax-like solid which is substantially insoluble in all ordinary solvents. When smaller amounts of hydrogen sulfide are used, the reaction products remain liquid. Although it is advantageous to obtain liquid or easily soluble solid reaction products, the solid, difficultly soluble products may also be used in accordance with my invention by melting the solid, dispersing the melted solid in a brine or other aqueous medium with agitation and introducing the dispersion into the annulus of the well to be treated. The degree of dispersion and the stability thereof may be improved by adding dispersing agents and stabilizing colloids, as is known in the art.

While the products of spontaneous reaction of hydrogen sulfide and an aqueous solution of formaldehyde, as set forth hereinabove, may be used with good effect, it is preferred to employ the reaction products obtained by reacting hydrogen sulfide and an aqueous solution of formaldehyde under controlled conditions. Under these conditions, even if the amount of hydrogen sulfide is such as to react completely with all of the formaldehyde, the products obtained are

aqueous oily liquids rather than wax-like solids and are readily dispersed in the well fluids. Thus, I have found that if the reaction temperature, having regard to the time of the reaction as fully described hereinbelow, is not permitted to exceed about 80° F., liquid reaction products are obtained even if the formaldehyde solution is saturated with hydrogen sulfide. A reaction temperature of 40° to 45° F. has yielded excellent reaction products.

I have also found that the reaction products obtained by reacting an aqueous solution of formaldehyde with hydrogen sulfide at low temperatures, below about 80° F., will be liquid if the time of the reaction does not exceed about 30 hours. Thus, clear solutions of the completely reacted formaldehyde-hydrogen sulfide reaction product were obtained at a reaction temperature of 80° F. and a reaction time of 6 to 8 hours. Clear solutions were also obtained at a reaction temperature of 60° to 65° F. and a reaction time of 30 hours. If slightly higher temperatures prevailed for this period of reaction, the product solidified. Similarly, when the reaction continued for a longer time, say 48 hours or longer, at the 65° F. reaction temperature, the product again solidified.

From the foregoing, it will be observed that in order to obtain liquid reaction products of aqueous formaldehyde and hydrogen sulfide, the reaction temperature must be correlated with the reaction time. At the higher temperatures of reaction not exceeding about 80° F., short periods of reaction, on the order of 6 to 8 hours, are used. At lower temperatures, say 60° to 65° F., a reaction period of 30 hours is permissible. At temperatures of 40° to 45° F. and below, liquid products will also be obtained, but, obviously, at the lower temperatures longer periods of time, not in excess of about 30 hours, will be required to completely react the formaldehyde with hydrogen sulfide. From the above, the proper temperature and reaction time to select to yield liquid reaction products will be obvious to those skilled in the art.

However, I have found that unless the above aqueous oily liquid reaction products are maintained after their formation at temperatures below about 60° to 65° F., they gradually harden on standing at ambient temperatures above 60° to 65° F. over a period ranging from several hours to about 25 days to form wax-like products, similar in nature to the hydrogen sulfide-formaldehyde reaction products obtained by saturating aqueous formaldehyde with hydrogen sulfide without controlling the reaction temperature, except that they are more soluble in the ordinary solvents. Since under many conditions of field use, it is difficult, if not impossible, to maintain the low temperatures necessary to prevent solidification of the oily liquid reaction products, I have found it desirable to stabilize such products against becoming solid. However, it should be understood that these solid products are also excellent corrosion inhibitors and may be used as such in accordance with my invention either by dissolving them immediately in a solvent such as acetone or alcohol or by melting the solids and dispersing them in a brine or other aqueous medium and injecting the solution or dispersion in the well to be treated. Nevertheless, it is desirable to employ the liquid reaction products, and to this end another aspect of my invention resides in the stabilization of such liquid products against solidification.

In accordance with this aspect of my invention, stabilized liquid reaction products of hydrogen sulfide with aqueous formaldehyde are obtained by reacting hydrogen sulfide with aqueous formaldehyde under the controlled conditions of time and temperature disclosed hereinabove to obtain an aqueous oily liquid reaction product, and substantially immediately after completion of the reaction adding to the reaction product a water-miscible oxygen-containing organic solvent. Such solvents include such water-miscible oxygenated solvents as methyl, ethyl, isopropyl and butyl alcohols, ethylene glycol, diethylene glycol, glycerol, the monomethyl, ethyl and butyl ethers of ethylene glycol, acetone, methyl ethyl ketone, dimethylal, ethylene glycol monoacetate, the monoethyl and butyl ethers of diethylene glycol, furfuryl alcohol, beta ethoxy ethyl acetate, and 1,4 dioxane. Mixtures of the above solvents may also be employed, particularly good results having been obtained with mixtures of acetone and dioxane and mixtures of acetone, dimethylal and methanol.

In general, the amount of solvent added to the aqueous oily liquid reaction product is at least about 30 per cent by volume. Amounts of solvent less than about 30 per cent by volume will not exert any significant effect in preventing the formation of the solid wax-like product from the oily liquid product. It is preferred to employ about 50 to 60 per cent by volume of the solvent. While larger amounts of solvent may be employed, it is uneconomical to do so since no additional stabilizing effects appear to be obtained.

It should be noted that while all of the above solvents have some effect in preventing the formation of solids, not all of them are equally effective. For example, when ethylene glycol was employed as the stabilizing solvent in an amount of 50 per cent by volume, solid formation was encountered after 18 hours storage at 80° F. With a 50 per cent by volume solution in isopropyl alcohol, the first precipitation of solids began after 6 days' storage at 76° to 80° F. With a 50 per cent by volume solution in a mixture of 46 per cent acetone, 40 per cent dimethylal and 14 per cent methanol by volume, precipitation did not begin until after 24 days' storage at 82° F. With a 40 per cent by volume solution of the aqueous oily liquid reaction product in 60 per cent by volume of a 50 : 50 mixture of acetone and 1,4 dioxane, precipitation of solids did not take place for a period of one year when stored under field conditions where the ambient summer temperatures reached as high as 120° F. The above described mixed solvent, viz., acetone and dioxane, is my preferred stabilizing material.

In order to demonstrate the effectiveness of the reaction products herein described, panels of mild steel strips, polished and weighed, were immersed in samples of a sulfide brine for 65 hours. The brine employed was from the Arbuckle Lime Zone, Kansas, having a pH of 6, an H_2S content of 500 milligrams per liter, and a specific gravity of 1.025. After immersion in the brine for 65 hours the steel strips were cleaned with dilute inhibited hydrochloric acid, washed in acetone, dried and re-weighed. In the following tables, the loss of weight due to corrosion is shown in weight loss per unit area and in the degree of protection obtained by the inhibitors. The degree of protection is calculated by the following formula:

$$\frac{W_1 - W_2 \times 100}{W_1}$$

wherein W_1 is the loss in weight per unit area with the uninhibited brine and W_2 is the loss in weight per unit area with the same brine containing an inhibitor.

As shown in the following tables, there were determined the corrosive effects of (1) an uninhibited brine, (2) the same brine containing formaldehyde, and (3) the same brine containing the H_2S-formaldehyde reaction products described herein. In Table 1, the H_2S-formaldehyde reaction products shown were obtained by reacting a 37 per cent by weight aqueous solution of formaldehyde with 2, 8 and about 25 per cent by weight of hydrogen sulfide, respectively (the latter being designated as saturated with H_2S), without controlling the reaction temperature, which was in the vicinity of 100° F. In Table 2, the H_2S-formaldehyde reaction product shown was obtained by saturating a 37 percent aqueous solution of formaldehyde with hydrogen sulfide at a temperature of 45° F. for a period of 16 hours until all the formaldehyde was reacted. The product obtained remained liquid for 24 hours at 45° F., but became semi-solid when warmed to 70° F. The semi-solid was quite soluble in alcohol and acetone, and a solution of semi-solid in an equal volume of alcohol was used in the tests.

The designation "p. p. m." in the following tables always refers to the parts per million of formaldehyde ether as such or combined in the reaction product with hydrogen sulfide. Thus, when used in connection with an H_2S-formaldehyde reaction product, it indicates the total amount of formaldehyde, i. e., that combined with the designated amount of H_2S plus any unreacted formaldehyde that may be present.

Table 1

	Corrosion Wt. Loss, mgm./cm.[2]	Degree of Protection, Percent
Uninhibited Brine	1.52	none
Brine Containing 0.01% by Vol. 37% Formaldehyde (40 p. p. m. of Anhydrous Formaldehyde)	0.93	39
Brine Containing 0.05% by Vol. 37% Formaldehyde (200 p. p. m. of Anhydrous Formaldehyde)	0.77	49
Brine Containing 0.05% Formaldehyde Reacted with 2% H_2S[1] (200 p. p. m.)	0.71	53
0.05% Formaldehyde Reacted with 8% H_2S[1] (200 p. p. m.)	0.70	54
0.05% Formaldehyde Saturated with H_2S[2] (200 p. p. m.)	0.70	54

[1] Heat of reaction caused temperature to reach near 100° F. in a few minutes.
[2] Reaction temperature went somewhat above 100° F. Solution became semi-solid near end of reaction and waxy-solid on cooling. This solid was liquefied by heat and measured into brine, where it was dispersed by agitation.

Table 2

	Corrosion Wt. Loss, mgm./cm.[2]	Percent Protection
0.001% by Vol. of H_2S Formaldehyde Reaction Product (2.0 p. p. m.)	0.38	75
0.0025% by Vol. of H_2S-Formaldehyde Reaction Product (5.0 p. p. m.)	0.38	75
0.005% by Vol. of H_2S-Formaldehyde Reaction Product (10.0 p. p. m.)	0.40	73
0.01% by Vol. H_2S-Formaldehyde Reaction Product (20.0 p. p. m.)	0.40	73

As may be seen from the above tables, the hydrogen sulfide-formaldehyde reaction products reduce corrosion to a much greater extent than equivalent amounts of formaldehyde. Com-

paring the effects of the H_2S-formaldehyde reaction products of Table 1 with those shown in Table 2, it will be apparent that the latter greatly reduce the amount of corrosion and that much smaller amounts of the inhibitor, as much as 100 times smaller, may be used to obtain greater protection against corrosion.

The preferred corrosion inhibitor of my invention was subjected to an extensive field test in a well producing brine that contained both hydrogen sulfide and carbon dioxide. A solution in a mixture of acetone and dioxane of an aqueous oily liquid reaction product of formaldehyde and hydrogen sulfide in the proportions by volume of 30 per cent acetone, 30 per cent dioxane and 40 per cent reaction product was employed for the test. The solution was added daily down the well annulus over a period of substantially a year in the ratio of 1 quart to each 200 barrels of brine produced, and was flushed down with about 5 gallons of well fluid from the bleeder. Prior to the addition of the inhibitor solution to the well, weighed mild steel test coupons were installed in the bottom hole below the pump and strainer and also in the flow line from the well, and the well produced for 6 days. Thereafter, the injection of inhibitor solution was begun and the test was continued for 84 days before the coupons were removed from the well. During the test period the well was shut down for 13 days and received no treatment with inhibitor during that time. It was unnecessary during the test to pull the rods, tubing and pump and the coupons remained undisturbed for the duration of the test. An examination of the coupons pulled from the well at the end of the coupon test period showed an average protection against corrosion of 86 per cent throughout the well, although the brine produced from the well was acidic and contained carbon dioxide and hydrogen sulfide. Prior to the test, this same well showed severe corrosion, and pulling jobs to replace corroded rod, tubing and pump were frequent. Thus prior to treatment, there was an average of 1.33 pulling jobs per month over a period of a year. After treatment in accordance with my invention, the average number of pulling jobs over a period of a year was reduced to 0.416 per month.

The corrosion inhibitor employed in the above test is typically prepared as follows. Sixteen and one-quarter (16.25) pounds of a commercial 25 per cent by weight aqueous formaldehyde solution having a specific gravity of 1.16 at 60°/60° F. were placed into a 2-gallon bottle and hydrogen sulfide was vigorously bubbled therethrough at a temperature of 42° to 45° F. for a period of 30 hours. A gain in weight of 15.4 per cent, based on the aqueous formaldehyde was obtained. The aqueous oily liquid reaction product was then immediately diluted with a 50 : 50 mixture by volume of acetone and dioxane in the proportion of 40 parts by volume of reaction product and 60 parts by volume of the mixed solvent. The resulting product remained stable without precipitating any solids for about a year under storage conditions in the field. In the field test described above, the daily dosage of formaldehyde-hydrogen sulfide reaction product was 3.5 p. p. m., expressed as formaldehyde.

It will be understood that by "liquid reaction products," "oily liquid reaction products" or "aqueous oily liquid reaction products," as used herein, I mean those oily liquid reaction products of aqueous solutions of formaldehyde with hydrogen sulfide which form a homogeneous aqueous solution with the water contained in the aqueous formaldehyde; that is, the water which is present in the aqueous formaldehyde reactant does not separate and is not separated from the liquid reaction products.

The amounts of the hydrogen sulfide-formaldehyde reaction products to use in accordance with my invention are, in general, such as are sufficient to retard the corrosive attack on metal equipment of the well by aqueous well fluids containing sulfides or carbon dioxide, or mixtures thereof. As little as 2.0 parts per million, expressed as the amount of formaldehyde, can be used with very satisfactory results, although larger amounts can also be used with good effect. Ordinarily not more than 20 p. p. m. of the reaction product, expressed as formaldehyde, will be required. It will be understood that the term "parts per million" as used herein and in the appended claims refers to the parts of reaction product, expressed as total formaldehyde, per million parts of the effluent brine produced through the well tubing.

In treating a well in accordance with my invention, the reaction products of formaldehyde and hydrogen sulfide are introduced into the well annulus and are dispersed in the well fluids being produced. When the treatment of my invention is first applied to old equipment in a well producing corrosive brine, it is desirable to wash the old equipment with an inhibited acid prior to using the hydrogen sulfide-formaldehyde reaction products described herein. Such acid treatment will remove both iron sulfide and iron oxide scale and will enhance the effects observed when the hydrogen sulfide-formaldehyde inhibitor is used for preventing further corrosion.

It is not necessary that wells be treated continuously in accordance with my invention. Daily or even semi-weekly dosage down the well annulus will prove sufficient in most cases. This is believed to be due to the fact that the oily and wax-like reaction products of formaldehyde and hydrogen sulfide have an affinity for metal surfaces and are quite largely adsorbed on the metal well equipment very quickly after addition to the well annulus. Metal surfaces coated with the reaction products resist wetting by water for considerable periods and show a preferential affinity for oil. This was illustrated by shaking water-wetted pieces of polished steel in solutions of crude oil and brine. When the oil and brine were first shaken with a small amount of the reaction products of this invention, the steel became oil-wet very quickly. On the contrary, when the experiment was performed under identical conditions but not using the reaction products of this invention, the steel became oil-wet after a much longer period or remained in the water-wet condition. This action of the reaction products of my invention is to be contrasted to that of formaldehyde which has been observed to pass quickly through sour oil wells, essentially in the state of the original, unreacted formaldehyde.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

I claim:

1. The method of inhibiting corrosive attack of metal equipment by aqueous well fluids containing sulfides, carbon dioxide or mixtures thereof which comprises separately preparing a reaction product of an aqueous solution of form-

aldehyde and hydrogen sulfide under controlled conditions including a reaction temperature not exceeding about 80° F. and a reaction time not exceeding about 30 hours to obtain an aqueous oily liquid reaction product, adding to said product an amount of a water-miscible oxygen-containing organic solvent to obtain a solution of said product in said solvent containing at least about 30 per cent by volume of said solvent, and then dispersing in said well fluids a small amount of said solution sufficient to retard said corrosive attack.

2. The method of claim 1, wherein said solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, diethylene glycol, glycerol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, acetone, methyl ethyl ketone, dimethylal, ethylene glycol monoacetate, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, furfuryl alcohol, beta ethoxy ethyl acetate, dioxane and mixtures thereof.

3. The method of inhibiting corrosive attack of metal equipment by aqueous well fluids containing sulfides, carbon dioxide or mixtures thereof which comprises dispersing in said well fluids a small proportion of a solution in a 50 : 50 mixture by volume of acetone and dioxane, of a preformed aqueous oily liquid product of reaction, at a reaction temperature of 42° to 45° F. and a reaction time of 30 hours, of a 25 per cent by weight aqueous solution of formaldehyde and hydrogen sulfide, said solution containing 60 per cent by volume of the mixture of acetone and dioxane, and the amount of said reaction product being sufficient to retard said corrosive attack.

4. The method of claim 3, wherein such an amount of hydrogen sulfide is used as to result in a gain in weight based on the aqueous formaldehyde of about 15 per cent, and the amount of said reaction product is equivalent to 3.5 parts expressed as formaldehyde, per million parts of said fluids.

5. A composition of matter effective for inhibiting corrosive attack of metal equipment by aqueous well fluids containing sulfides, carbon dioxide or mixtures thereof which comprises a solution in a water-miscible oxygen-containing organic solvent of a preformed aqueous oily liquid product of reaction, at a reaction temperature not exceeding about 80° F. and a reaction time not exceeding about 30 hours, of an aqueous solution of formaldehyde and hydrogen sulfide, said solution containing at least about 30 per cent by volume of said solvent.

6. The composition of claim 5, wherein said solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, diethylene glycol, glycerol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, acetone, methyl ethyl ketone, dimethylal, ethylene glycol monoacetate, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, furfuryl alcohol, beta ethoxy ethyl acetate, dioxane and mixtures thereof.

7. A composition of matter effective for inhibiting corrosive attack of metal equipment by aqueous well fluids containing sulfides, carbon dioxide or mixtures thereof which comprises a solution in a 50 : 50 mixture by volume of acetone and dioxane, of a preformed aqueous oily liquid product of reaction, at a reaction temperature of 42° to 45° F. and a reaction time of 30 hours, of a 25 per cent by weight aqueous solution of formaldehyde and hydrogen sulfide, said solution containing 60 per cent by volume of the mixture of acetone and dioxane.

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