Aug. 20, 1940. H. L. KOHLER 2,212,270

PROTECTIVE COATED ARTICLE

Filed Nov. 9, 1938

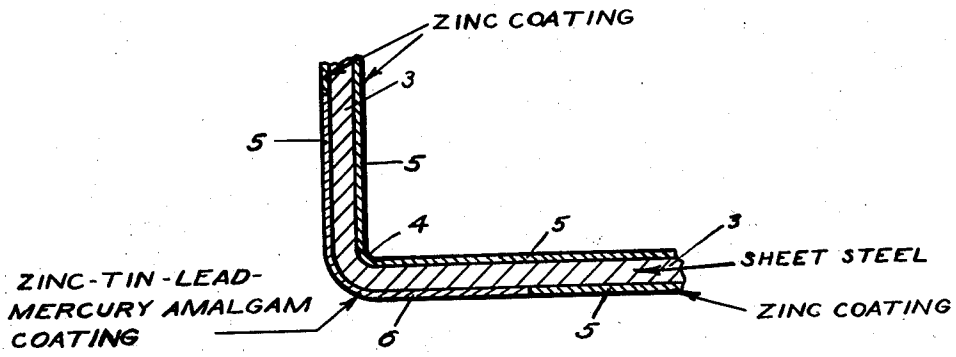


Fig. 1

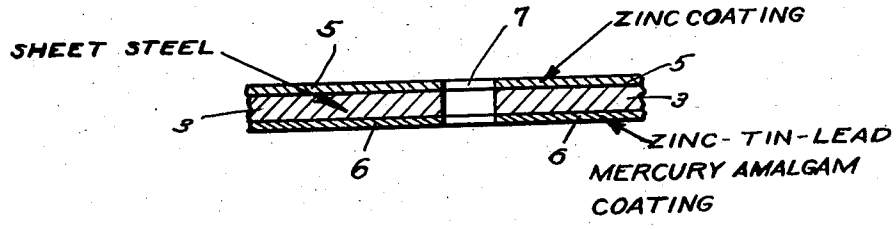


Fig. 2

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Patented Aug. 20, 1940

2,212,270

UNITED STATES PATENT OFFICE

2,212,270

PROTECTIVE COATED ARTICLE

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Application November 9, 1938, Serial No. 239,729

11 Claims. (Cl. 29—181)

My invention relates to protective coated articles, and more particularly to sheet metal articles provided with a protective coating. This application is a continuation in part of my copending application Serial No. 144,029, filed May 21, 1937, issued March 21, 1939, as Patent 2,150,929.

A difficulty that has always existed in the utilization of galvanized metallic sheets for making certain articles out of the same, has been that the galvanizing coating is not sufficiently resistant to corrosion under certain conditions to make the practical use thereof possible. An attempt to overcome this difficulty has been made by providing a heavier galvanizing coating on the sheet. The heavy zinc coating thus provided, however, has the disadvantage that, when the sheet is bent, the coating at the bend would crack and tend to peel or flake off. As a result, although the sheet as a whole was provided with a heavy galvanizing coating over its entire surface before being fabricated, the bending of a sheet to form a flange or a seam thereon, frequently damaged the galvanizing coating on the sheet so seriously that it would render the coating partially ineffective, on the outside of the bends required to form the flanges, or seams. Consequently the advantage of the heavy galvanizing coating on the sheet was largely lost, this being true because, at the point at which the galvanizing coating was caused to be damaged, or ruptured, by bending, the sheet would be, for practical purposes, no better than an uncoated sheet, as far as resistance to oxidation, or other corrosion, was concerned. While many attempts have been made to overcome this difficulty, as by a hot dipping process after the article has been formed from the galvanized sheet, for example, this is difficult to accomplish and requires expensive equipment, if any large sheet metal article is to be galvanized after fabrication by such a dipping process.

It is a purpose of my invention to provide means for overcoming the above mentioned difficulty with galvanized sheets that have a heavy coating of galvanizing thereon, and at the same time provide a sheet that is much more resistant to corrosion over the entire area thereof, if such resistance over such entire area is desired, than is possible with ordinary zinc coatings provided by the usual galvanizing process. I accomplish this by providing a mercury-lead-zinc amalgam coating on the sheet, or a mercury-lead-tin-zinc amalgam coating on the sheet, said coating being applied to any area thereof that may be desired.

My improved protective coating may be utilized to give better protection than zinc against certain types of corrosion, or corrosion due to certain causes, either over the entire area of a metallic sheet, or over the entire area of one side thereof, or over the entire area of a fabricated sheet metal section, or one side of such a section, if this should be desired, and is particularly adapted for use at and adjacent the bends in a fabricated sheet, whereby any rupture in the galvanizing coating that may have occurred during fabrication, from any of the fabrication steps, will be closed and the sheet protected at such bends, or other fabricated portions thereof, more effectively than was the case before the bending, or other operation, thereon, that damaged, or ruptured, the protective zinc coating on the sheet originally.

It is a further purpose of my invention to provide a protective coating of a lead-zinc-mercury amalgam that has the same appearance as the zinc coating originally on the sheet, as obtained by the usual galvanizing process. It is also a purpose of my invention to provide a protective coating of a zinc-tin-lead-mercury amalgam that has the same appearance as the zinc coating originally on the sheet, as obtained by the ordinary galvanizing process. Galvanized metallic sheets have a characteristic spangled appearance. It is highly desirable to maintain this spangled appearance of the sheets after my improved coating has been placed thereon. This is accomplished by utilizing a paste-like lead-mercury amalgam, or a paste-like lead-tin-mercury amalgam, which is applied to the sheet in a manner that the structural characteristics of the zinc coating on the sheet are not changed. My improved protective coating will resist every kind of corrosion better than does the galvanized sheet before having the treatment thereof, whereby my improved coating is produced, and will also provide a coating that will be more resistant to corrosion than the heavy galvanizing coating applied to such sheets, or fabricated sheet metal sections, at bends therein, or other places where ruptures in the heavy galvanizing coating might and do frequently occur. As the term "fabrication" is used herein, it means any bending, cutting or punching operation, or any other operation on the sheet, that may be performed thereon after the same has been rolled and galvanized.

It is a particular purpose of my invention to provide a protective coating on a sheet that includes zinc and lead, or zinc, tin and lead, in

which the lead content is much greater than has been possible to previously obtain by any previously known methods. Zinc and lead will not combine readily under ordinary circumstances, and the percentage of lead that will alloy with the zinc of a zinc coating is relatively small and such alloys are difficult to produce. By providing an amalgam coating including zinc and lead, however, a much higher percentage of lead can be obtained in a coating on a sheet, and the same is true where a lead-tin solder is used in such an amalgam to produce a zinc-lead-tin-mercury amalgam coating on the finished product. As lead is particularly resistant to certain kinds of corrison, it is very desirable to have a relatively large lead content in a coating on a sheet that is subjected to certain kinds of corrosion. Tin is also more resistant to corrosion than zinc, and if a certain percentage of the lead is supplanted by tin, substantially the same results will be obtained as if the full percentage of lead were included in the coating. Lead being relatively inexpensive, and having the desirable characteristics mentioned, is preferred in the amalgam coating for these reasons.

Other objects and advantages of my invention will appear as the description of the same proceeds. I desire to have it understood, however, that I do not intend to limit myself to the particular details described, except as defined in the claims.

Fig. 1 is a fragmentary sectional view on a greatly enlarged scale, showing my improved amalgam coating applied to a sheet having a bend therein, and

Fig. 2 is a similar view, showing my improved amalgam coating applied to a sheet otherwise fabricated than by bending.

Referring in detail to the drawing, in Figs. 1 and 2 the metallic body portion of the sheet, which is usually steel or iron, is indicated by the numeral 3. The sheet shown in Fig. 1 is bent at 4 and the bend may cause damage to the zinc coating ordinarily on the galvanized sheet on the outer side of the bend substantially at the outer corner thereof. The zinc coating provided on the sheet is indicated by the numeral 5 and the amalgam coating around the outside of the bend and adjacent said bend in the sheet is indicated in Fig. 1 by the numeral 6.

In Fig. 2 the same numerals are applied to the zinc coating and the amalgam coating, but instead of showing a sheet with a bend therein, the sheet is shown as being fabricated by punching a hole 7 therein, this being merely illustrative of some fabrication operation that may be performed on the sheet that may damage the ordinary zinc galvanizing coating thereon. The coating, indicated by the numeral 6, may be either a lead-zinc-mercury amalgam coating, or a lead-tin-zinc-mercury amalgam coating, as is explained below.

My improved protective coating is provided on galvanized sheets that have been fabricated to the desired size and shape, by bending, die-shaping, cutting and punching operations, or any of these that may be necessary to produce the article, or sections of an article, of the desired shape from the galvanized sheet of metal. After the sheet has been fabricated, it is cleaned at the places at which the protective coating is to be provided thereon, usually by means of dilute hydrochloric acid, or a solution of tin chloride, or antimony chloride, or lead chloride, or zinc chloride, or cyanide of soda. This cleaning solution may be applied with a brush or swab of some character, and the excess may be removed with a cloth, or any other suitable means. When it is desired to apply the protective coating only at or adjacent a ruptured area on a galvanized sheet, or an area that may have been damaged to the extent of injuring the protective coating, or rupturing the same, the galvanized sheets are cleaned only on the outer sides of all bends therein, or any other area at which the coating may have been ruptured, or damaged, and areas adjacent these bends, or other areas where the damage may have occurred. A zone at the place at which the rupture in the zinc coating may exist will thus be cleaned, and also a zone on each side thereof.

A putty-like amalgam of mercury and lead, or of mercury and lead and tin, is made up prior to cleaning the sheets, or is made up in quantity to be used whenever necessary, said amalgam having such proportions of the metal, or metals, amalgamating with the mercury therein, to the quantity of mercury therein, as to produce a soft putty-like material of the consistency of thick paste, or cream. The proportions of mercury and lead, or of mercury and lead and tin, that are used to produce this soft putty-like material, will vary somewhat, dependent upon whether lead alone is used, or lead and tin is used, and also upon the atmospheric temperature existing, as the material must, of course, be of the soft creamy putty-like character at the temperature at which it is to be applied to the sheet. Thus in the winter time, when a lower temperature is encountered, both in the atmosphere and in the material of the sheets themselves, a larger proportion of the mercury to the lead, or lead and tin, must be used to produce the soft putty-like coating material. I have found that 65% of mercury and 35% of lead by weight will produce an amalgam of the desired consistency in the summer time, while in the winter time, when the temperatures are exceedingly low, it is frequently necessary to utilize an amalgam made for this purpose, that is made up of one part by weight of lead, to three or four parts by weight of mercury.

Substantially the same proportions are necessary where lead-tin solder is used, except in the case of a lead-tin solder which contains 33⅓% lead and 66⅔% tin, which solder has a lower melting point than does the tin contained therein. Such a solder can be combined with the mercury in the proportions of at least 40% of the solder to 60% of the mercury in the summer time, or under ordinary warm weather conditions, to produce such a soft putty-like amalgam as desired. The relative proportions of the metal, or metals, amalgamating with mercury, that have to be utilized, are dependent upon the melting points of the metals that are amalgamated with mercury and the temperature encountered. Thus, if the mercury is heated when the lead is added thereto, as much as 50% lead can be included in the putty-like amalgam, and as much as 50% of a lead-tin solder, containing 33⅓% lead and 66⅔% tin can be included in an amalgam and produce a putty-like, soft creamy material for application to a sheet. If more than 50% of lead or such solder is amalgamated with the mercury while heated, the amalgam will not remain in a putty-like condition at the temperature at which it can be practically applied to the sheet.

In making up the putty-like, or creamy, paste-like amalgam, it is necessary that the lead that

is to be dissolved in the mercury, or amalgamated therewith, is in a finely divided condition when it is to be amalgamated with the mercury. The lead can be in the form of any small particles, such as shavings, turnings, cuttings, or in the form of a powder or granules. The finely divided lead is stirred into the quantity of mercury that is to be utilized to make the amalgam in the proportions necessary, substantially within the limits above referred to. When a lead-tin-mercury amalgam is to be made, solder is ordinarily used for the lead and tin content of the amalgam, and if desired, the solder can also be utilized in such finely divided form as set forth above. If the solution, or amalgamation of the solder with the mercury, is to take place at a practical rate at room temperatures, such division into fine particles is necessary. If an unusually large amount of solder or lead is to be incorporated in the amalgam, it is necessary to heat the mercury to cause the material to be dissolved. Also, if the solder is to be amalgamated with the mercury without finely dividing the same, or in other words, if relatively large pieces of the solder are to be dissolved, or amalgamated, with the mercury, the mercury must be heated to accomplish this in a practical manner. Inasmuch as the melting point of the solder is somewhat below that of the vaporization point of the mercury, heating up to the melting point of the solder can be utilized to get quick solution of the solder in the mercury, even if the solder is in a large piece, or large pieces, without loss of any of the mercury by vaporization. Whenever either the lead content, or the lead-tin solder content, desired in the amalgam, is above that readily amalgamating with the mercury at room temperature, the mercury may be heated for this purpose, keeping the temperature of the mercury well below that at which it would vaporize.

The soft putty-like amalgam of lead and mercury, or of lead, tin and mercury, produced as above described, is applied to the cleaned zone, or area, of the galvanized sheet, by a brushing or rubbing operation, the soft putty-like amalgam being brushed, or rubbed, onto the cleaned area of the sheet with a cloth, or in a similar manner. This rubbing or brushing operation spreads the lead-mercury amalgam, or the lead-tin-mercury amalgam, as the case may be, over the cleaned area of the sheet and causes a thin layer thereof to adhere to the outer surface of the zinc coating on the sheet, and in case there is a rupture or damaged area in the sheet, from which the zinc has been entirely, or substantially entirely, removed, the lead-mercury amalgam, or lead-tin-mercury amalgam, as the case may be, will adhere to the sheet at this ruptured area also. As soon as the amalgam contacts the zinc coating on the sheet, it begins to act thereon to amalgamate the zinc in the zinc coating with some of the mercury in the amalgam. Accordingly, in brushing the amalgam back and forth over the ruptured area, some of the zinc of the galvanizing coating will be caused to be spread over the ruptured area, and any loose flakes, or particles, of zinc will be dissolved in the lead-mercury amalgam, or lead-tin-mercury amalgam, as the case may be, amalgamating with the mercury in such amalgam.

The action between the zinc and the lead-mercury amalgam, or the lead-tin-mercury amalgam, will continue until the amalgam has penetrated the entire zinc coating of the sheet down to, at least, the ferrous zinc alloy at the surface of the iron, or steel, of the sheet. As the zinc amalgamates with the mercury, the resulting amalgam will gradually become stiffer and harder, as the greater the amount of other metal amalgamated with the mercury, the harder and stiffer the amalgam will become. As a result, the penetration of the zinc by the lead-mercury amalgam will eventually produce a zinc-lead-mercury amalgam protective coating on the sheet over the entire surface to which the lead-mercury amalgam has been applied, which has lost the soft character of the lead-mercury amalgam and will become as hard as the zinc coating originally on the sheet. Similarly, the penetration of the zinc by the lead-tin-mercury amalgam will eventually produce a zinc-lead-tin-mercury amalgam protective coating over the entire surface to which this amalgam was applied, which has lost the soft character of the lead-tin-mercury amalgam, and will become as hard as the zinc coating originally on the sheet. It has been found that the use of an amalgam containing lead produces more rapid hardening of the amalgam coating on the sheet, than when a tin-mercury amalgam, for example, is used.

Thus, while the amalgam, when first placed on the sheet, will be soft enough that it can be rubbed off on the fingers to a certain extent, in the case of both the lead-mercury amalgam, and the lead-tin-mercury amalgam, after at least twenty-four hours, the coating at the area to which the amalgam has been applied will be hard enough that none of the same will rub off and the sheet can be handled without any damage to the coating, just as readily as was the case with the zinc coating on the sheet originally. In fact, the lead-mercury amalgam, or lead-tin-mercury amalgam, when utilized as above described, will produce a protective coating on a sheet that will be practically as hard as was the zinc coating on the sheet originally before such treatment, at approximately twenty-four hours after application of the amalgam to the sheet. The sheet will, after the coating has become hard, have substantially the same appearance as it did before any amalgam was applied thereto, and none of the coating can be rubbed off, even though it may be rubbed persistently for a considerable period of time. The coating will have the characteristic spangled appearance of the zinc coating originally on the sheet. This indicates that the application of the putty-like amalgam to the sheet that has been previously galvanized, while resulting in the dissolving of the zinc on the sheet, in the mercury of the amalgam, does this in such a gradual manner that the liquefaction of the coating material on the sheet takes place at such a slow rate through the thickness of the zinc coating that the structure of the zinc coating on the sheet is not altered, although the composition changes from substantially pure zinc to a zinc-lead-mercury amalgam, or a zinc-lead-tin-mercury amalgam, as the amalgamating process proceeds through the coating. The sheet will accordingly have substantially the same appearance two or three days after the amalgam was applied thereto as it had before any application of amalgam thereto.

While my improved coating is provided particularly to prevent corrosion at ruptures in the zinc coating of a galvanized sheet, it is obvious that such a coating can be provided advantageously, under certain conditions, not only to the area of a sheet on the outer side of a bend at and adjacent said bend, but to the entire surface of a

sheet, that is innermost when put in place as a wall portion of a container that is subjected to the corrosive action of sulphuric acid, or other sulphur compounds, which are ordinarily found in oil tanks, or similar receptacles. These sulphur compounds cause a corrosive action on the zinc coating of the sheet as ordinarily provided in oil and similar tanks. However, by utilizing my protective coating, including the lead-mercury amalgam, or lead-tin-mercury amalgam, and applying it to the inner surface of an oil tank, or the sections of an oil tank, made up of sheets that have been bent, cut and punched, this undesirable corrosive action is avoided entirely.

The tendency of the sulphur compounds, when acting on either of the amalgam coatings described, is to cause the mercury in the amalgam to form a protective film on the surface that is exposed to the action of the dilute sulphuric acid, or hydrogen sulphide, or other sulphur compounds, this causing some slight loss of some of the other metals from the coating, such as the zinc, lead and tin, but the mercury arresting this loss substantially immediately, due to the film forming action that it has.

While it is immaterial whether the amalgam coating is of the same composition throughout, it has been found that if the soft putty-like amalgams, above referred to, are utilized, some of the mercury in the amalgams will amalgamate with the zinc immediately, forming either a zinc-lead-mercury amalgam, or a zinc-tin-lead-mercury amalgam, as the case may be, and some of the lead-mercury amalgam, or some of the lead-tin-mercury amalgam, as the case may be, will be present without any zinc in it at first, this being on the top surface of the coating. However, if the amalgams above referred to are left in contact with the zinc coating for twenty-four hours, or more, and an excessive amount of the amalgam is not used, sufficient of the mercury will amalgamate with the zinc that all of the zinc will become amalgamated with the mercury, and the resulting coating will be, in the case of the use of a lead-mercury amalgam, a lead-zinc-mercury amalgam, and in the case of the use of a lead-tin-mercury amalgam, the resulting coating will be a zinc-lead-tin-mercury amalgam, from the outer surface thereof to at least the ferrous zinc alloy at the surface of the metal of the sheet. Due to the fact that the zinc requires a much larger amount of mercury to be amalgamated with the same to produce a soft putty-like amalgam, than does lead or tin, this amalgamation of the mercury with the zinc, when completed, causes the coating to have a hard character, similar to that of the zinc, instead of a soft putty-like character, such as the amalgams had before these were applied to the sheet.

When a putty-like amalgam containing 35% lead and 65% mercury by weight, is utilized for application to a galvanized sheet that has a coating thereon of zinc that amounts to one ounce per running square foot, or one-half ounce per square foot surface on each side of the sheet, the amalgam will contain approximately 74.4% zinc, 10.2% lead, and 15.4% mercury. If a putty-like amalgam containing 60% mercury and 40% by weight of a tin-lead solder that is made up of 33⅓% lead and 66⅔% tin by weight, is utilized for application to a galvanized sheet that has a zinc coating, such as above referred to, thereon, the amalgam resulting will contain approximately 70.85% zinc, 7.77% tin, 3.38% lead and 17.5% mercury. With a heavier coating of zinc, the percentage of zinc will, of course, be higher, and of course, the percentage of lead, or lead and tin, will be less in the case of an amalgam being used that contains a larger percentage of mercury. As in all cases the amount of zinc in the amalgam coating resulting on the sheet will be over 50%, the coating will retain the characteristics of a zinc coating to a considerable extent, but will be modified in its characteristics considerably by the mercury contained therein, and to a lesser extent by the lead, or tin and lead, contained therein.

As zinc coatings as heavy as two and one-half ounces per running foot are encountered on galvanized sheets, the resulting coating, where a putty-like amalgam of 35% lead and 65% mercury by weight is applied to such sheet, will contain approximately 87.5% zinc, 4.4% lead, and 8.1% mercury by weight, and where a putty-like amalgam of 40% solder and 60% mercury by weight, is applied to such a sheet, the solder being 33⅓% lead and 66⅔% tin by weight, the resulting coating on such a sheet will contain approximately 83.34% zinc, 2.22% lead, 4.44% tin and 10% mercury by weight.

Due to the variations in the percentages of lead and mercury, or lead, tin and mercury, that can be used under different temperature conditions, and variations in thickness of the zinc on the sheet, the percentage of zinc in the lead-zinc-mercury amalgam coating can be varied between 74 and 88%, the lead between 2.5 and 14%, and the mercury between 6 and 22% by weight, and the desired characteristics of the coating obtained, while in the lead-tin-zinc-mercury amalgam coating the zinc can vary between 70 and 84%, the lead between one and 8%, the tin between one and one-half and 10% and the mercury between 8 and 24% by weight, and the desired characteristics of the coating maintained.

It is highly desirable that the spangled appearance of the coating on the sheet, such as it has when galvanized, be maintained, as this coating has a desirable appearance from the standpoint of the user, and due to the familiarity of the user with the spangled appearance of galvanized sheets, any destruction of this appearance is found to be objectionable from a commercial standpoint.

What I claim is:

1. A galvanized sheet having a bend therein and having a zinc coating thereon on the side thereof lying on the inside of said bend and an amalgam coating including zinc, lead and mercury on the side thereof lying on the outside of said bend at and adjacent said bend, said amalgam containing at least 70% zinc and having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet.

2. A metallic sheet having a zinc-tin-lead-mercury amalgam coating thereon, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet and containing over half zinc.

3. A galvanized sheet having a bend therein and having a zinc-tin-lead-mercury amalgam coating on the side thereof lying on the outside of said bend at and adjacent said bend, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet and containing over half zinc.

4. A galvanized metallic sheet having a zinc coating on a portion of the area thereof and a coating of an amalgam including zinc, lead and

mercury on the remainder of the area thereof, said amalgam coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet and containing over half zinc.

5. A metallic sheet having a coating of an amalgam including zinc, lead and mercury thereon, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet and containing at least 70% zinc.

6. A galvanized metallic sheet having a zinc coating on a portion of the area thereof and a coating of an amalgam including zinc, tin, lead and mercury on the remainder of the area thereof, said amalgam coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet and containing more than half zinc.

7. A metallic sheet having a coating thereon of an amalgam comprising from 5 to 35 parts zinc and from 1 to 4 parts mercury to one part lead by weight.

8. A metallic sheet having a coating thereon of an amalgam including from 74 to 88 per cent zinc by weight, lead and mercury.

9. A metallic sheet having a coating thereon of an amalgam including from 70 to 84 per cent zinc by weight, tin, lead and mercury, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet.

10. A metallic sheet having a coating thereon of an amalgam including from 70% to 84% zinc by weight, tin, lead, and from 8% to 24% mercury by weight, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet.

11. A metallic sheet having a coating thereon of an amalgam including from 70% to 84% zinc by weight, from 1½% to 10% tin by weight, from 1% to 8% lead by weight, and from 8% to 24% mercury by weight, said coating having at least as great a proportion of mercury at its exposed surface as adjacent the metal of the sheet.

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