United States Patent Office 2,862,842 Patented Dec. 2, 1958

2,862,842

PRETREATMENT OF IRON OR STEEL BASE FOR SINGLE COAT VITREOUS ENAMELING

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No Drawing. Application May 9, 1958
Serial No. 734,113

20 Claims. (Cl. 148—6)

This application is a continuation-in-part of our co-pending application Serial No. 677,813, filed August 13, 1957, now abandoned.

This invention relates to a novel method of pretreating an iron or steel base to prepare the same for single coat vitreous enameling.

In order to obtain acceptable adherence between an iron or steel article and a light colored enamel it has been customary in the enamel trade for many years to utilize a so-called ground coat which contains certain dark colored adherence-promoting oxides such as cobalt oxide, nickel oxide or manganese oxide. Since such ground coats are dark in color, it has been necessary to employ one or more cover coats of light colored enamel over the ground coat in order to achieve an acceptable light colored enamel finish. Although the ground coat technique does not entirely solve the problem of eliminating surface defects in enameled articles, nevertheless, it it still widely used on a commercial scale in spite of the many efforts which have been devoted to the problem of eliminating the ground coat and providing a commercially acceptable single coat enameling procedure.

Obviously, the elimination of the ground coat in the production of light colored enameled articles would result in a substantially lower cost of production both from the viewpoint of materials used and also by the elimination of one or more process steps. Moreover, it has been found that iron or steel articles having only a single coat of enamel are highly resistant to chipping and crazing of the enameled surface as compared with multi-coated articles having two or more enamel coats.

Various attempts have been made to improve the adherence of cover coat enamels to iron or steel articles without the use of a ground coat. For example, certain of the prior art workers have devised special compositions for the enamel frit or special techniques in the preparation of the enamel slip which are said to improve adherence. Other workers in the art have advocated the provision of a substantial degree of surface roughness in the metal prior to enameling, the desired roughened surface being obtained by mechanical means, by scale annealing, by chemical pickling, or by some combination thereof. Although it is true that certain of these proposals may result in some degree of improvement in enamel adherence under some conditions, none of them has been consistently satisfactory in commercial practice or sufficiently economical to make possible the omission of dark colored adherence-promoting oxides from the enamel coat as a general practice. Thus, to a large extent the industry has continued to employ the dark colored ground coat and one or more superimposed cover coats of light colored enamel.

Another approach to the problem has been by the use of enameling steels of special composition designed to eliminate surface defects and to improve the metal-enamel bond. Certain of these special steels have been highly successful to the extent that excellent single coat enamel adherence is obtained with a greatly reduced

occurrence of surface defects and without the use of the conventional dark colored ground coat. However, wide scale use of such special steels is often limited largely by reason of their obviously higher cost.

Although enameled articles are subject to many different types of surface defects which are associated with poor adherence, perhaps the most critical requirement for a satisfactory single coat enamel is freedom from fishscaling. Fishscaling is the expulsion, popping off or chipping off of small fishscale shaped pieces of the fired enamel coating and may occur during processing or some time after processing. According to the current theories, fishscaling is said to be caused by the release of hydrogen gas from the metal base upon cooling, the hydrogen presumably originating by the chemical reduction at enameling temperatures of water contained principally in the enamel frit. Generally speaking, fishscaling is associated with unsatisfactory enamel adherence so that the enamel coat is disrupted at various places under the excessive localized hydrogen gas pressure in the metal base. Consequently, the minimum prerequisite of any acceptable single coat enameling technique is substantial freedom from fishscaling.

A primary object of our invention is to provide a novel, relatively simple, and inexpensive solution to the long existent problem of producing enameled articles having a satisfactory enamel bond with only a single cover coat of vitreous enamel thereby eliminating the necessity for a dark colored ground coat.

Another object of the invention is to provide a novel method of pretreating an iron or steel base in order to prepare the same for enameling, said method being adapted to provide satisfactory single coat enamel adherence with a wide variety of irons or steels.

An additional object of the invention is to provide a novel iron or steel base for vitreous enameling with only a single light colored enamel cover coat which is substantially free of dark colored adherence-promoting oxides and having satisfactory adherence without fishscaling or other surface defects.

We have found that satisfactory single coat enamel adherence and unusually good surface appearance are consistently obtained by pretreating the iron or steel base as follows: (1) providing on the surface of the metal base an oxide coating comprising molybdenum oxide (MoO_3) or anhydride either alone or with other oxides, particularly nickel and cobalt oxides, and (2) heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in the base takes place and thereby diffusing the surface of the base with molybdenum. A third step which is optional comprises pickling the thus treated base under relatively mild conditions sufficient to "clean" the metal surface but without severely etching or roughening the same.

In the first step of the process the molybdenum oxide or anhydride may be deposited as such or formed in situ on the surface of the iron or steel base. Although molybdenum oxide alone gives excellent results, there are advantages in using a mixture of molybdenum oxide with nickel oxide or cobalt oxide or both. The preferred embodiment of the invention involves the use of molybdenum and nickel oxides together. However, it is also within the scope of the present invention to use molybdenum oxide in combination with titanium, antimony, and tungsten oxides which are the subject matter of our copending application Serial No. 686,287, filed September 26, 1957.

One method of providing the oxide coating on the iron or steel base is to form a suspension or dispersion in water or other suitable liquid medium of the oxide or oxides in finely divided or powdered form and then apply

the liquid coating material to the surface of the base by any convenient technique such as spraying, brushing, roll-coating, dipping, etc. Usually, water will be the most convenient liquid medium but other liquid vehicles such as glycerine, light oils, etc. can be used. In the case of an aqueous medium it is usually advantageous to employ an added dispersing or suspending agent, such as starch or various surface active agents, in order to form a relatively stable suspension or dispersion of the finely divided oxide in the aqueous liquid. We have found that corn starch is highly satisfactory and economical for this purpose.

It is also within the scope of the invention to provide the oxide coating on the metal surface by means of a solution or suspension of a compound or salt which can be decomposed or oxidized to yield the desired oxide in situ. For example, ammonium molybdate or molybdic acid can be deposited on the metal surface and is readily decomposable merely by heating to form the desired molybdenum trioxide. In the case of the preferred embodiment of the invention utilizing molybdenum and nickel oxides together, a very convenient technique comprises forming an aqueous solution of nickel nitrate or chloride or other water soluble nickel salt and ammonium molybdate or molybdic acid whereby to obtain a molybdenum-nickel complex. Ammonium hydroxide should also be added in order to maintain the molybdenum-nickel complex in solution. The resultant aqueous solution is applied to the metal surface and is thermally decomposed to yield the desired mixture of molybdenum and nickel oxides.

The quantity of oxide provided on the metal surface is not highly critical but a certain minimum amount of oxide must be present in order to realize the benefits of the invention to any practical degree. For obtaining satisfactory enamel adherence it has been found that sufficient molybdenum oxide should be present to yield, upon reduction thereof by reaction with the iron in the base, from about 0.05 to about 0.4 gram of molybdenum per square foot of surface. In other words, the contained molybdenum content of the oxide coating should be from about 0.05 to about 0.4 gram per square foot of surface. Although larger amounts may be used, there appears to be no additional benefit justifying the use of greater amounts of molybdenum oxide. Similarly, in the case where nickel or cobalt oxide is also used, it appears that sufficient nickel oxide or cobalt oxide should be present to yield from about 0.05 to about 0.2 gram of nickel or cobalt per square foot of surface in order to realize the enhanced benefits attributable to the combined metals but above this level no appreciable improvement is noted. In the case of the combination of molybdenum and nickel oxides, the relative amounts of the two oxides may vary but we have obtained best results when the total contained nickel and molybdenum is from about 0.1 to about 0.4 gram per square foot of surface. Within this range the relative proportions may vary considerably but generally we prefer to use a minimum of 0.05 gram per square foot of each metal. For example, good results are obtained with amounts of from about 0.05 gram per square foot of each metal up to about 0.2 gram per square foot of each, but equally good results are also obtained using about 0.05 gram per square foot of one of the metals with from about 0.05 to about 0.35 gram per square foot of the other metal.

Following the formation of the oxide coating on the surface of the iron or steel base, either by direct application of the oxide or in situ formation of the same, the next essential step of the invention is to heat the oxide coated base to an elevated temperature and for a sufficient time to obtain reduction of the oxide or oxides by reaction with the iron in the base. This step may sometimes be referred to as a heat treating or diffusing step. Broadly speaking, the temperature range for this step of the process may be from about 1150° F. to about

2000° F. dependent upon the nature of the base and the time of treatment. For example, in the case of enameling iron it is preferred to use a relatively high temperature which may be from about 1400° F. to about 2000° F. and it will usually be most economical to conduct the heating step in a continuous manner such as in a continuous normalizer so that the heating time is short, e. g. from about 1 to about 5 minutes. On the other hand, in the case of a mild steel base (0.05 to 0.10% carbon) the heating step can be conducted at a relatively lower temperature, e. g. from about 1150° F. to about 1300° F., and for a much longer period of time on the order of 3 to 12 hours. In the case of the latter procedure, it will be found that a batch type box annealing operation is the most economical technique. Thus, it will be understood that as far as enamel adherence is concerned the time and temperature of the heating step of the invention are correlative factors so that for any given type of iron or steel base substantially equivalent results may be obtained at conditions of high temperature-short time or low temperature-long time. However, the choice of temperature for the heating step may also be dictated by the necessity of developing certain desired mechanical or structural properties in the iron or steel base. Thus, in the case of enameling iron, which has a lower carbon content (0.02 to 0.04%) than mild steel, it is generally preferred to carry out the heating step, at least in part, in the 1400–2000° F. range heretofore mentioned so as to obtain optimum mechanical or structural properties in the final product.

Although under very favorable circumstances, it is possible to carry out the heating and reducing step in a somewhat oxidizing atmosphere, it will readily be understood that the heating of the oxide coated base should preferably be conducted in a non-oxidizing atmosphere, i. e. either neutral or reducing. A wide variety of atmospheres which are either neutral or reducing to a predetermined degree are well known in connection with the various normalizing, annealing, and heat treating operations which are frequently carried out in the steel-making art. However, generally speaking, such atmospheres comprise specially prepared mixtures of inert gases containing none or a certain predetermined amount of hydrogen which determines the reducing character of the atmosphere.

As previously indicated, it will be desirable in most cases to subject the resultant pretreated base to a rather mild or light pickling operation solely for the purpose of "cleaning up" the metal surface in order to provide a salable product. However, it is to be understood that this pickling step is of relatively short duration so that there is no appreciable etching action or production of surface roughness of the nature which has previously been thought by some investigators to influence the adherence of a subsequent enamel coating. The usual acid pickle liquors may be employed, e. g. a suitable pickling operation in accordance with the present invention comprises treating the base with a solution of 8% sulfuric acid for a period of about one minute. However, it is to be understood that this final pickling step is not an indispensable part of the invention and in any given operation it may be omitted entirely since it has no significant effect on the subsequent enamel adherence. As a matter of practice, the enameler at a later date will ordinarily give the product a light pickle and a conventional nickel strike or flash before application of the enamel coat.

It has been postulated by some investigators that the presence of FeO is essential during the firing of vitreous enamels on iron bases because of the fact that FeO is soluble in iron and also forms a silicate with the enamel component thereby acting as a mutual bonding agent. Since the firing of the enamel takes place in an oxidizing atmosphere, it will be apparent that, in the absence of some regulating factor, either Fe_2O_3 or Fe_3O_4

or FeO may be formed. It is believed that the formation of Fe_2O_3 during the enamel firing is highly detrimental and will result in poor adherence since this compound is not soluble in iron. Hence, it is our hypothesis that the molybdenum which is formed on or diffused into the metal surface of the iron or steel base by the above-described technique controls the oxidation of the iron of the base so that Fe_2O_3 is not formed during the firing of the enamel and so that Fe_3O_4 or preferably FeO are present to insure an adequate bond. However, it will be understood that the invention is not limited by this proposed explanation of the results obtained.

The adherence of vitreous white or light colored cover coat enamels to surfaces so treated is equal to or better than that ordinarily obtained in the enameling trade through the use of ground coats. Therefore, the fish-scaling difficulties ordinarily encountered when attempting to apply white or light colored vitreous enamel coatings to ordinary ferrous base metals are entirely eliminated. In addition, the technique of the present invention eliminates, to a large extent, the other more common vitreous enamel defects such as blistering, pitting, copper-heading, and so forth, which are objectionable from an appearance standpoint. However, even the best white or light colored enamel coating tends to have a certain uneven appearance caused by many small pits, craters, or depressions in the enamel surface. This effect, which is sometimes referred to as "fuzziness" or a "gassy" appearance, can be tolerated to some extent but has been most prevalent heretofore in cases where the enamel adherence is quite good and has been least noticeable in cases where the enamel adherence is poor. For reasons which we do not entirely understand, the use of a molybdenum oxide coating as herein described minimizes to a large extent or eliminates "fuzziness" thereby giving a superior surface quality while at the same time preserving good adherence.

The presence of nickel in the coating in addition to molybdenum promotes a somewhat higher degree of enamel adherence than is obtained with the molybdenum alone. Also, we have found that a reduced amount of the combined nickel and molybdenum coating is required as compared with molybdenum alone for equivalent adherence.

In order to illustrate some of the features of the invention, but not by way of limitation, the following specific examples are presented.

Example I

The test specimens comprised a cold reduced enameling iron having the following composition on a weight percent basis: .035% C, .07% Mn, .007% P, .029% S, .08% Cu.

The test specimens were subjected to the treatment hereinafter described and a white cover coat enamel was then applied by spraying and firing for approximately five minutes at about 1500° F. The enamel frit had the following composition on a weight percent basis:

	Percent
SiO_2	42.8
B_2O_3	15.8
Na_2O	10.5
K_2O	3.7
TiO_2	19.6
Al_2O_3	1.5
LiO_2	0.6
MgO	0.9
P_2O_5	2.8
F	1.8
	100.0

The enamel slip was prepared by milling the following ingredients in the indicated proportions:

	Grams
Frit	3400
Clay	84.5
Sodium nitrite	4.25
Sodium aluminate	8.5
Bentonite	17.0
Potassium carbonate	8.5
Gum tragacanth	2.1
Water	1300

After milling to a fineness of about 2 grams on a 200 mesh screen, the following mill additions were made:

	Grams
Sodium nitrite	2.1
Urea	12.7

After enameling, the test specimens were evaluated for adherence by the well known impact test, the results being designated as poor, fair, good or excellent by visual examination.

The cold reduced test strip was first treated for the removal of rolling oil by vapor degreasing or by means of an alkaline cleaner. The oil-free strip was then given an oxide coating by immersing the strip for a brief time in an aqueous solution containing 400 grams of ammonium molybdate per liter of water. After removal from the treating solution the test strip was allowed to drain and dry leaving a coating on the strip containing about 0.3 gram per square foot of contained molybdenum. The thus treated strip was then subjected to heat treatment for five minutes in a reducing atmosphere containing 5% hydrogen at a temperature of from about 1400 to about 1850° F. whereby the ammonium molybdate on the strip was thermally decomposed to molybdenum oxide which was in turn reduced by the iron in the strip to effect diffusion of molybdenum in the surface of the test strip.

Upon being enameled with white cover coat enamel in the manner described above, the test specimens were found to display excellent adherence with a highly satisfactory surface appearance characterized particularly by a marked absence of fuzziness.

Exactly the same results were obtained using a neutral atmosphere comprising nitrogen for the heating and reduction step.

In cases where the present invention is to be practiced with existing equipment it may not always be convenient to utilize a vapor degreasing or alkalin cleaning step for the removal of rolling oil from the cold reduced strip. In such case, we have found that the oily strip may be treated directly with the ammonium molybdate or other molybdenum oxide-providing liquid, but it will usually be desirable to incorporate in the treating liquid a suitable wetting agent to facilitate uniform wetting of the oily surface of the strip with the treating liquid. For example, to the aqueous solution of ammonium molybdate described above may be added about 0.1% of a non-ionic surface active agent of which many different kinds are well known. We have obtained good results with Kyro EO which is sold by Procter & Gamble Distributing Co. and comprises an alkylphenolethylene oxide condensate. Following the application of the ammonium molybdate treating solution, the strip is then placed in or passed through an oxidizing furnace at a temperature on the order of 700° F. for a very brief period of time which is merely sufficient to burn off the rolling oil but without causing any appreciable degree of scaling or oxidation of the metal. Thereafter, the treated strip is subjected to the same heating step in a neutral or reducing atmosphere as described above. Excellent enamel adherence is again obtained with remarkably good surface appearance.

Example II

The same procedure as described in Example I was followed with the exception that the coating liquid comprises an aqueous solution containing about 75 grams nickel

nitrate, about 67 grams ammonium molybdate, and about 165 mls. of ammonium hydroxide per liter of water. The resultant coating on the test strip provided about 0,3 gram of contained molybdenum and 0.15 gram of contained nickel per square foot of surface. Excellent adherence and highly satisfactory surface appearance were again realized.

When using oily cold reduced strip without degreasing or cleaning, the aqueous treating solution has added thereto about 0.1% of a suitable wetting agent such as Kyro EO and the procedure is otherwise the same as described in Example I.

Example III

The same procedure described in connection with Example I was followed except that instead of an aqueous solution of ammonium molybdate we employed a starch-containing suspension of molybdic oxide (MoO_3), also known as molybdic anhydride. The starch suspension contained 25 grams per liter of corn starch and 40 grams per liter of molybdic oxide. Excellent adherence and good surface appearance were obtained in the enameled test specimens.

In the case where the suspension was applied directly to the oily cold reduced strip, the suspension also contained about 0.1% Kyro EO and the same procedure as described in Example I was followed.

Example IV

The procedure was the same as described in Example II with the exception that instead of an aqueous solution of nickel nitrate and ammonium molybdate we employed an aqueous starch suspension containing about 25 grams per liter of corn starch, about 20 grams per liter of molybdic oxide, and about 10 grams per liter of nickel oxide.

In the case where the suspension was applied directly to the oily cold reduced strip, we obtained best results by using a suspension containing about 25 grams per liter of corn starch, about 54 grams per liter of nickel oxide, about 32 grams per liter of molybdic oxide, about 20 grams per liter of nickel nitrate, and about 0.1% Kyro EO as a wetting agent. The presence of nickel nitrate in the suspension, although not essential, appears to provide better wetting of the metal surface. The procedure was otherwise the same as described in Example I.

In every instance, excellent enamel adherence was obtained with highly satisfactory surface appearance.

Example V

In this instance the test specimens were 10" x 10" panels of 20 gauge mild steel (about .09% C) in the full hard condition. Molybdenum oxide and molybdenum oxide-nickel oxide coatings were applied to various test panels in the same manner as described in Examples I and II. To simulate a box annealing operation, the test panels after coating were bolted together in stacks between a pair of steel plates in order to obtain a tight packing. The stacks were then heat treated, some in a neutral atmosphere and some in a reducing atmosphere, for 12 hours at 1200° F. followed by slow cooling.

The test panels as treated above were given a conventional cleaning, pickling, and nickel flash and a white cover coat enamel was applied and fired as heretofore described. Good to excellent adherence was obtained with optimum results being realized in the case of the molybdenum oxide-nickel oxide coated specimens.

We claim:

1. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising molybdenum oxide, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs.

2. The process of claim 1 further characterized in that said temperature is within the range of from about 1150° F. to about 2000° F.

3. The process of claim 1 further characterized in that said base comprises an enameling iron and said heating step is carried out in a continuous operation at a temperature of from about 1400° F. to about 2000° F.

4. The process of claim 1 further characterized in that said base comprises a mild steel and said heating step is carried out in a batch operation at a temperature of from about 1150° F. to about 1300° F.

5. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating of molybdenum oxide and at least one other oxide selected from the group consisting of the oxides of nickel and cobalt, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1150° F. to about 2000° F. sufficient to effect reduction of the oxide by reaction with the iron in said base.

6. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating of molybdenum and nickel oxides, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1150° F. to about 2000° F. sufficient to effect reduction of the oxides by reaction with the iron in said base.

7. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of applying to the surface of the metal base a liquid suspension comprising molybdenum oxide, and thereafter heating the coated base in a non-oxidizing atmosphere at a temperature within the range of from about 1150° F. to about 2000° F. and for a time sufficient to effect reduction of the oxide by the iron in said base.

8. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of applying to the surface of the metal base a liquid coating material comprising a molybdenum compound capable of being thermally decomposed to molybdenum oxide, and thereafter heating the coated base in a non-oxidizing atmosphere at a temperature within the range of from about 1150° F. to about 2000° F. and for a time sufficient to effect decomposition of the molybdenum compound to molybdenum oxide and reduction of the oxide by the iron in said base.

9. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising molybdenum oxide, heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs, and thereafter pickling the base.

10. The process of claim 7 further characterized in that said suspension comprises molybdenum and nickel oxides.

11. The process of claim 7 further characterized in

that said liquid suspension comprises a dispersion of the oxide in water with starch as a dispersing agent.

12. The process of claim 8 further characterized in that said coating material comprises a molybdenum-nickel complex capable of being thermally decomposed to yield molybdenum and nickel oxides.

13. The process of claim 8 further characterized in that said coating material is formed by combining a water soluble nickel salt with said molybdenum compound in aqueous solution so as to form a molybdenum-nickel complex capable of being thermally decomposed to yield molybdenum and nickel oxides.

14. The process of claim 8 further characterized in that said coating material comprises an aqueous solution of nickel nitrate, ammonium molybdate, and ammonium hydroxide.

15. The process of claim 1 further characterized in that said oxide is present on the metal surface in an amount sufficient to provide, after reduction thereof, from about 0.05 to about 0.4 gram of molybdenum per square foot of surface.

16. The process of claim 6 further characterized in that said oxides are present on the metal surface in an amount sufficient to provide, after reduction thereof, from about 0.1 to about 0.4 gram of total molybdenum and nickel per square foot of surface.

17. An iron or steel base having a coating produced according to the process of claim 1.

18. An iron or steel base having a coating produced according to the process of claim 5.

19. A process for enameling an iron or steel base with a single cover coat of a light colored vitreous enamel comprising the steps of providing on the surface of the metal base a coating comprising molybdenum oxide, heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs, applying to the surface of the base a cover coat of light colored vitreous enamel which is substantially free of dark colored adherence-promoting oxides, and firing said enamel thereon.

20. A process for enameling an iron or steel base with a single cover coat of a light colored vitreous enamel comprising the steps of providing on the surface of the metal base a coating of molybdenum oxide and at least one other oxide selected from the group consisting of the oxides of nickel and cobalt, heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1150° F. to about 2000° F. sufficient to effect reduction of the oxide by reaction with the iron in said base, applying to the surface of the base a cover coat of light colored vitreous enamel which is substantially free of dark colored adherence-promoting oxides, and firing said enamel thereon.

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