Nov. 3, 1953 C. O. HOOVER 2,658,027

NEUTRALIZATION OF ACID CONSTITUENTS IN PETROLEUM

Filed Dec. 3, 1951 2 Sheets-Sheet 1

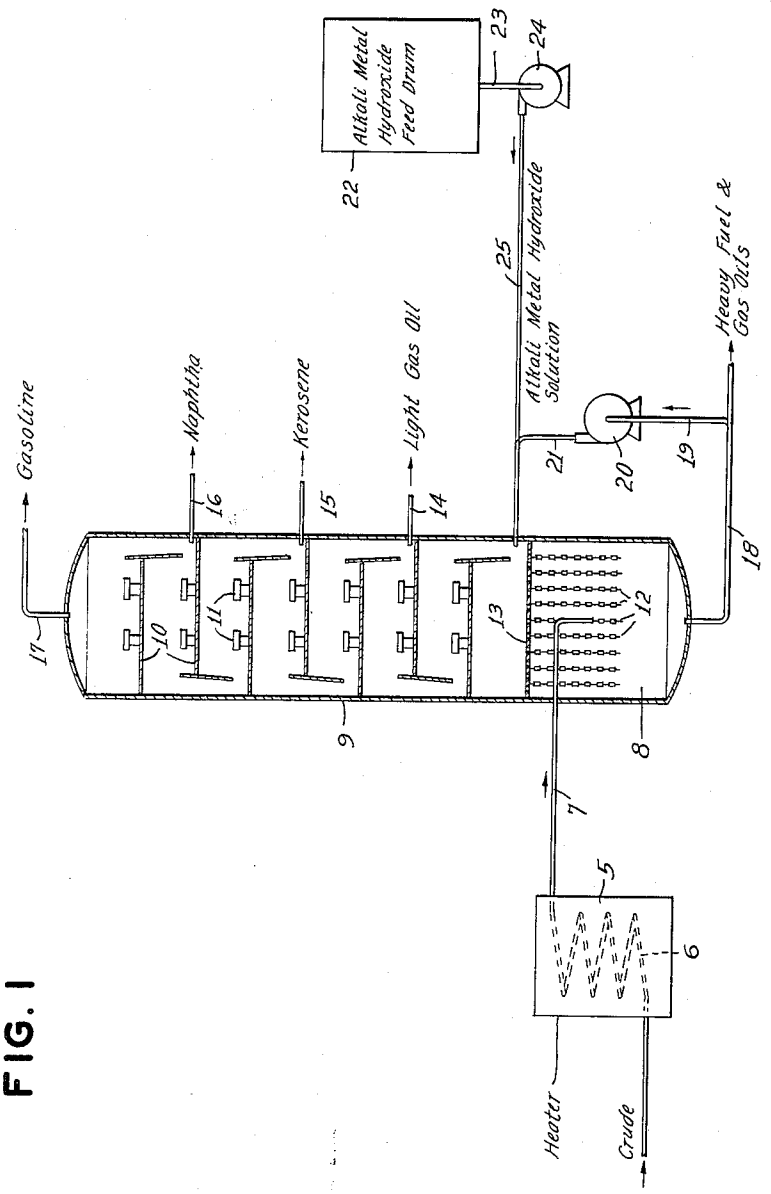


FIG. 1

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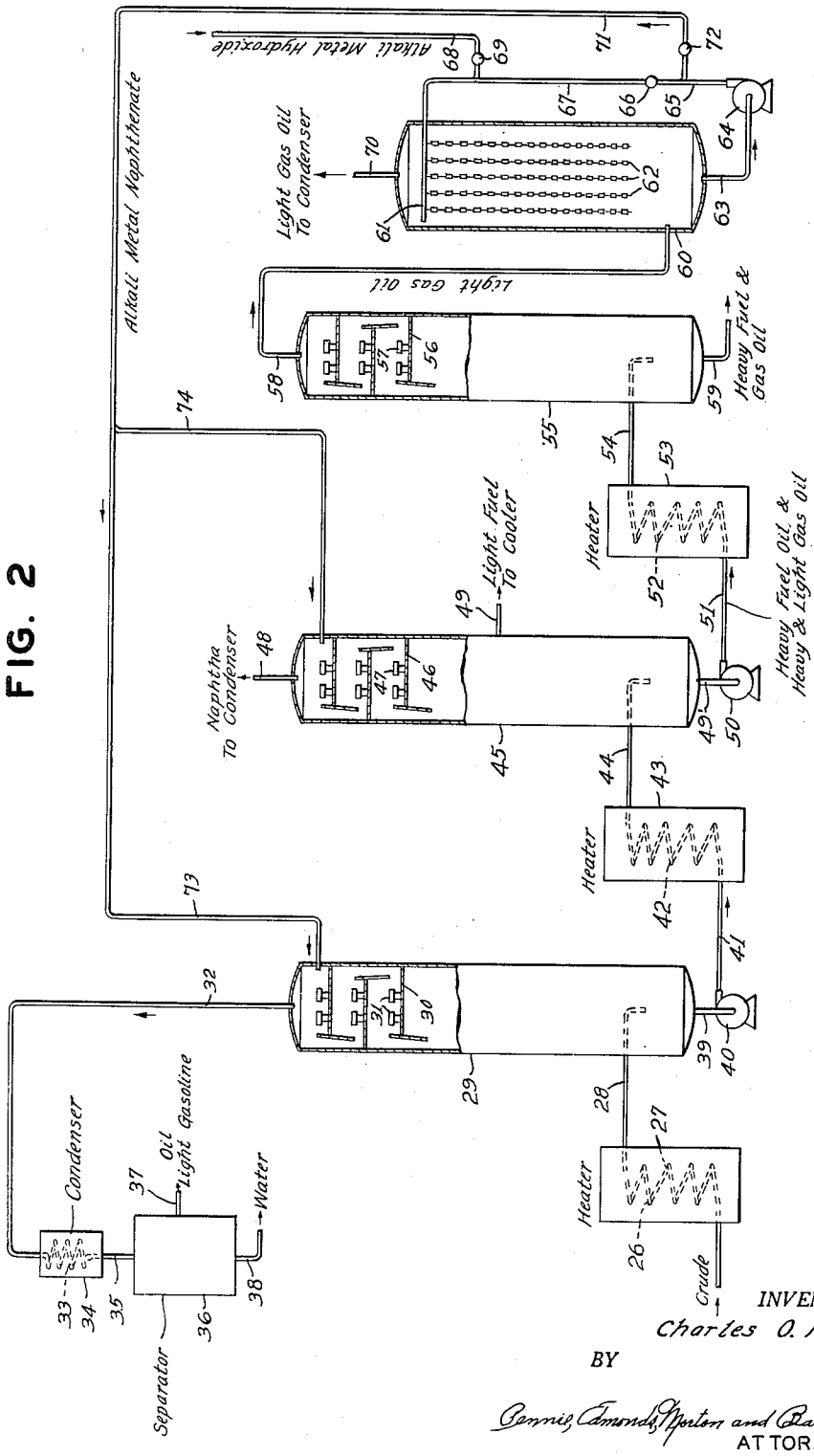
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FIG. 2



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NEUTRALIZATION OF ACID CONSTITUENTS IN PETROLEUM

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13 Claims. (Cl. 196—36)

1

This invention relates to the neutralization of acid constituents in petroleum hydrocarbon products, and particularly to the utilization of alkali metal compounds of organic acids to neutralize acid constituents of the oil, such as hydrochloric acid, the presence of which is due to the brine content of the oil; sulfurous acid and sulfuric acid which may result from oxidation of sulfur contained in the oil; hydrogen sulfide which may result from reduction of sulfur contained in the oil; etc. The neutralization of such inorganic acid constituents of petroleum products eliminates the common problem of corrosion which is a serious handicap in refining operations.

A primary object of this invention is to provide a method for neutralizing the acid constituents of petroleum hydrocarbons by contact thereof in the vapor phase with an alkali metal soap of an organic acid.

Generally stated, and in accordance with this invention, the method consists in directly contacting hydrocarbon vapors containing corrosive acid constituents with an alkali metal soap or soaps of an organic acid or acids, preferably in solution or in suspension in the petroleum hydrocarbon. The resulting action is to effect replacement of the weaker organic acid component of the alkali metal soaps by the relatively more strongly inorganic acid constituents in the hydrocarbon vapor, thereby effectively neutralizing the inorganic acid constituents, which are those chiefly responsible for corrosion of the distillation equipment. The organic acids which are freed by this exchange reaction may be recovered at a subsequent stage in the process by neutralization with an alkali metal hydroxide to re-form the organic acid soaps for re-use in the neutralization reaction, and to insure that the petroleum distillate is freed from any contained organic acid, as well as inorganic acid constituents.

Many crude petroleums contain naphthenic acids as one of the constituents thereof. If the particular hydrocarbon being treated is one containing naphthenic acids they may be used to react with the alkali metal hydroxide to form an alkali metal naphthenate to be used for the neutralizing of the inorganic acid constituents of the hydrocarbon. In the absence, originally, of naphthenic acids in the hydrocarbons undergoing treatment, naphthenic or other organic acid or acids sufficient to initiate the neutralization process may be supplied from extraneous sources, either in the form of the acids themselves or as alkali metal compounds thereof.

2

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and the accompanying drawing, in which

Fig. 1 illustrates diagrammatically a single flash system for the refining of petroleum embodying the invention; and

Fig. 2 is a similar illustration of a three-flash system also embodying the invention.

Referring to the drawing, 5 indicates a suitable heater including a coil 6 through which crude petroleum is passed for the purpose of raising its temperature to the neighborhood of 650°–750° F. The heated petroleum is delivered, through a pipe 7, into the lowest compartment 8 of a bubble column 9. The upper part of the column includes the usual trays 10 and bubble caps 11 through which the vapors rise in intimate contact with condensate flowing down over the trays 10. In the lower compartment 8, a plurality of chains 12 are suspended from the perforated plate 13 so that the liquid accumulating on the plate 13 trickles downwardly in a film-like stream over the chains, thus affording the maximum possible contact between the liquid and the vapors resulting from release of the heated petroleum into the compartment 8. The petroleum flashes into vapor which, after contact with the liquid on the chains, passes upwardly through the column. The vapor is separated selectively into light gas oil which is withdrawn through a pipe 14, kerosene which is withdrawn through a pipe 15, naphtha which is withdrawn through a pipe 16, and gasoline which escapes as vapor through a pipe 17 at the top of the column and passes to a condenser (not shown) where it is condensed to the liquid phase. Thus, in a single operation the petroleum is separated into several cuts affording the desirable constituents of the original crude petroleum.

The liquid accumulating in the bottom of the compartment 8 is heavy fuel and gas oil which is withdrawn through a pipe 18 and may be suitably treated for subsequent use. A portion of this oil is recirculated through a pipe 19, pump 20 and pipe 21 to the plate 13 for further contact with vapors in the compartment 8.

To accomplish the purpose of the invention, an aqueous solution of an alkali metal hydroxide is maintained in a tank 22 and is delivered through a pipe 23 to a proportioning pump 24 and thus fed at the desired rate through a pipe 25 to the pipe 21 where it mingles with the oil which is circulating therethrough and onto the plate 13. The alkali metal hydroxide in the

circulating oil reacts with the acid content of the vapors in the compartment 8, thereby removing the acids which are separated as neutral compounds in the oil accumulating in the bottom of the compartment 8 while the vapors, free from acid constituents, rise through the column 9. Thus, the various cuts removed from the vapors are free from acid constituents. The organic acid in the vapors (naphthenic acids of the hydrocarbon, if it originally contained naphthenic acids, or added organic acid if the hydrocarbon did not originally contain naphthenic acids, or naphthenic acids in sufficient amount) is readily separated as an alkali metal soap by the procedure described. Any hydrochloric acid which may be present as the result of brine in the oil likewise is neutralized, as is also any sulfur dioxide, sulfurous acid and sulfuric acid which may be the result of oxidation of sulfur contained in the oil, and any hydrogen sulfide which may be the result of reduction of sulfur contained in the oil. In any event, the prompt neutralization of such acid constituents prevents corrosion of the equipment which commonly requires replacement of many thousands of dollars of such equipment annually in the refining industry.

The oil recirculated from the bottom of compartment 8 to plate 13 will contain the alkali metal naphthenate or other soap formed by the neutralization reaction, and this material serves as a neutralizing agent for the inorganic acid constituents of the vapors released in compartment 8, the free naphthenic or other organic acids being released by reaction of the alkali metal soap with the more strongly acidic inorganic acid constituents. The free organic acids, being of relatively high boiling point, remain in the oil accumulating in the bottom of compartment 8 and are reconverted to the alkali metal soaps by reaction with the alkali metal hydroxide when commingled therewith in pipe 21 and on plate 13, the resulting oil solution or dispersion of alkali metal soaps being then contacted with additional vapors released in compartment 8 to repeat the neutralization reaction. Once the process is placed in operation, the continuous regeneration of the organic acid assures the neutralization of hydrochloric acid and other inorganic acidic materials which may be present in the oil, so that condensates formed from the treated vapors are free from such corrosive acidic materials.

Referring to Fig. 2 of the drawing, which shows a three-flash system, the crude petroleum is introduced through a coil 26 in a heater 27 where it is raised to a temperature of approximately 550° F. It passes through a pipe 28, into a bubble column 29 having the usual trays 30 and bubble caps 31. The heated petroleum flashes into vapor and passes upwardly through the column in contact with condensate produced on the trays 30. The effluent vapor is withdrawn through a pipe 32 at the top of the column, delivered to a coil 33 and a condenser 34 and thus passes into the liquid phase. It is delivered through a pipe 35 to a separator 36. Light gasoline is withdrawn through a pipe 37, and any water which may be present is separated and removed through a pipe 38.

The liquid formed on the trays 30 accumulates in the bottom of the tower 29 and is withdrawn through a pipe 39 and delivered by a pump 40 through a pipe 41 to a coil 42 in a heater 43 where the oil is heated to a temperature of approximately 625° F. It passes through a pipe 44 into a bubble tower 45 having the usual trays 46 and bubble caps 47. The vapor rises through the tower in contact with condensate on the trays 46 and escapes through a pipe 48 to a condenser (not shown). The condensate is naphtha and may be further treated or used for any suitable purpose. Light fuel oil may be withdrawn through a pipe 49 at an intermediate level of the bubble tower 45. The condensate in the tower 45 is withdrawn through a pipe 49' and delivered by a pump 50 through a pipe 51 to a coil 52 in a heater 53 where the oil is heated to a temperature of approximately 625°–750° F. It passes through a pipe 54 into a bubble tower 55 having trays 56 and bubble caps 57. The vapor rises through the trays, being partially condensed thereon. Vapor escapes through a pipe 58 at the top of the column. The condensate in the tower 55 is withdrawn through a pipe 59 and is heavy fuel and gas oil which may be used or subsequently treated.

To accomplish the purpose of the present invention, the light gas oil vapor withdrawn through a pipe 58 is delivered to a tower 60 having a perforated pipe 61 near its top and a plurality of chains 62 depending therefrom. The condensate in the tower 60 is withdrawn through a pipe 63 and delivered by a pump 64 through a pipe 65 controlled by a valve 66 and thence through a pipe 67 to the plate 61 at the top of the tower 60. An aqueous solution of alkali metal hydroxide is delivered through a pipe 68 controlled by a valve 69 to the pipe 67 and mingles with the oil. The aqueous solution of alkali metal hydroxide may be supplied through a suitable proportioning device (not shown) so as to be delivered in the proper amount to accomplish the object of the invention. The oil and the aqueous solution of alkali metal hydroxide trickle downwardly over the chains 62 in contact with the vapors in the tower 60 and neutralize the acid constituents thereof. Light gas oil vapor is withdrawn from the top of the tower 60 through a pipe 70 and delivered to a condenser (not shown). This product is free from acid constituents.

The organic acid of the petroleum, naphthenic acid, if the petroleum originally contained it, otherwise added organic acid, is neutralized by reaction with the alkali metal hydroxide supplied, as described, to produce an alkali metal soap of the organic acid. A portion of the oil containing the alkali metal soap and other neutralization products is withdrawn through a pipe 71 controlled by a valve 72, and branches 73 and 74 of the pipe 71 carry the oil containing the alkali metal soap into the bubble towers 29 and 45 at the tops thereof. The alkali metal soap readily reacts with hydrochloric acid, sulfur dioxide, sulfurous acid, sulfuric acid, and hydrogen sulfide, which may be present in the petroleum vapors, regenerating the organic acid and neutralizing the corrosive hydrochloric acid and other acidic materials which are particularly undesirable inasmuch as they cause the major portion of the corrosion in refining equipment. As the result of the operation as described, the released organic acid is carried over to again react with alkali metal hydroxide in the tower 60, so that the cycle is continuous. Once the process is placed in operation, the continuous regeneration of the organic acid assures the neutralization of hydrochloric acid and other acidic ma-

terials which may be present in the oil and the condensates are free therefrom.

As an example of the operation of the procedure as described in connection with Fig. 2 of the drawing, a naphthenic crude petroleum, at the rate of 18,000 barrels per day, with a salt content of 10 pounds per thousand barrels, was run through the apparatus. The sodium naphthenate was employed as the neutralizing agent. The separator water, before the sodium naphthenate was added to establish the cycle, had a pH of 1.2. During the operation as described in the present application, the pH of the separator water was 6.5 to 7.0, thus establishing the advantage of neutralization of the acid content in the manner described. Furthermore, no hydrogen sulfide was found in distillates or gases resulting from the operation.

To completely avoid all corrosion in the apparatus, 74.5 pounds of sodium hydroxide were used per day, making approximately 530 pounds of sodium naphthenate which was diluted with approximately 150 pounds of gas oil before use. This dilution occurs in the sodium naphthenate tower 30. Since the crude petroleum contained naphthenic acid, the only chemical which had to be added was sodium hydroxide. The procedure eliminated hundreds of dollars per day in corrosion and down-time costs.

If the crude is one which does not contain naphthenic acids, or does not contain them in sufficient amount, they, or oleic acid, stearic acid, linoleic acid, tall oil, resin acids, castor oil fatty acids, or hydrogenated hardened fats, either as such, or as alkali metal compounds, may be added to initiate the neutralization process. In such case they or any combination of them may be blended at any time in the liquid state at atmospheric or increased temperatures with the crude petroleum or any of the distillates thereof, prior to their vaporization, or they can be injected into the flow lines of the oil to be vaporized at any point before the oil reaches the vaporizing coils or other heaters, or they may be injected into the heating coils proper, or into the hot oil flow lines at the outlet of the heating coils up to the point where the oil is caused to react with the alkali metal hydroxide, or, in the case of the method of Fig. 2, into the soap-oil circulating line, up or down stream, from the point where the new caustic is injected.

Any of the organic acids mentioned above, either singularly, or any mixture of them, may first be vaporized extraneously and the vapors forced into the flow lines or the reaction tower or the soap-oil circulating line at the points mentioned. Very satisfactory results have been obtained in this manner.

If desired, the alkali metal hydroxide solution used to regenerate the alkali metal soap may be replaced by a slurry consisting of oil and granules of a solid alkali metal hydroxide. The reaction between the acid constituents in the oil and the added alkali seems to be equally efficient, whether the alkali is in water solution or in the solid state. The granule size of the caustic will ordinarily range from about 10-mesh down to fine powders.

Various changes may be made in the procedure as described and in the apparatus employed without departing from the invention or sacrificing the advantages thereof.

This application is a continuation-in-part of my pending application Serial No. 70,921, filed January 14, 1949, now abandoned.

I claim:

1. The method of neutralizing acid constituents of petroleum distillates which comprises vaporizing a petroleum distillate containing inorganic acid material, passing the vapor in intimate contact with an alkali metal organic acid soap with resultant neutralization of inorganic acid material, and thereafter condensing the vapor.

2. The method of claim 1 in which the vapor of the petroleum distillate is passed into intimate contact with an oil solution of the alkali metal soap.

3. The method of neutralizing acid constituents of petroleum distillates which comprises vaporizing a petroleum distillate containing an organic acid and inorganic acid material, passing the vapor in intimate contact with an alkali metal soap of an organic acid contained in said vaporized petroleum distillate with resultant neutralization of inorganic acid material, and thereafter condensing the vapor.

4. The method of neutralizing acid constituents of petroleum distillates which comprises vaporizing a petroleum distillate containing inorganic acid material, passing the vapor into intimate contact with an oil solution of an alkali metal naphthenate with resultant neutralization of inorganic acid material, and thereafter condensing the vapor.

5. The method of neutralizing inorganic acid constituents of petroleum distillates which comprises vaporizing a petroleum distillate containing inorganic acid material, passing the vapor into intimate contact with an alkali metal organic acid soap with resultant neutralization of inorganic acid constituents, and thereafter condensing the vapor.

6. The method of neutralizing acid constituents of petroluem distillates which comprises passing a vapor of a petroleum distillate containing an organic acid and inorganic acid material into intimate contact with an alkali metal hydroxide, thereafter condensing the vapor, and bringing the alkali metal soap produced by reaction of organic acid constituents with the alkali metal hydroxide into intimate contact with other portions of the vaporized petroleum to neutralize inorganic acid constitutents therein.

7. The method of claim 6 in which the vapor of the petroleum distillate is passed into intimate contact with an aqueous solution of the alkali metal hydroxide.

8. The method of claim 6 in which the vapor of the petroleum distillate is passed into intimate contact with a slurry of oil and granules of a solid alkali metal hydroxide.

9. The method of neutralizing acid constituents in petroleum distillates which comprises passing a vapor of a petroleum distillate containing naphthenic acid and inorganic acid material into intimate contact with an alkali metal hydroxide, withdrawing a condensate of the vapor containing an alkali metal naphthenate, and bringing the condensate into intimate contact with vapors from other portions of the petroleum distillate to neutralize inorganic acid constituents thereof.

10. The method of neutralizing acid constituents in petroleum distillates which comprises passing a vapor of a petroleum distillate containing naphthenic acid and inorganic acid material into intimate contact with an alkali metal hydroxide, withdrawing a condensate of the vapor containing an alkali metal naphthenate, recirculating a portion of the condensate with addi-

tion of alkali metal hydroxide for further contact with the vapor of petroleum distillate, and bringing the condensate not recirculated into intimate contact with vapors from other portions of the petroleum distillate to neutralize inorganic acid constituents thereof.

11. The method of neutralizing acid constituents of petroleum distillates which comprises vaporizing petroleum, rectifying the vapor by passing it upwardly in contact with condensate therefrom and an oil solution of alkali metal naphthenate, condensing the vapor, heating the liquid product of the rectification to vaporize it, repeating the operation with the resulting vapor, heating to vaporize the liquid product of the second rectification, rectifying the vapor, passing the vapor product of the third rectification in intimate contact with a multiplicity of streams of an aqueous solution of alkali metal hydroxide, withdrawing an oil solution of alkali metal naphthenate produced by such contact and returning the oil solution of alkali metal naphthenate for use in the first and second rectifications.

12. The method of neutralizing inorganic acid constituents contained in petroleum distillates which comprises adding an organic acid to the petroleum, vaporizing the petroleum, passing the resulting vapor into intimate contact with an alkali metal hydroxide, thereafter condensing the vapor, and bringing the alkali metal soap produced by reaction of organic acid constituents with the alkali metal hydroxide into intimate contact with other portions of the vaporized petroleum to neutralize inorganic acid constituents therein.

13. The method of neutralizing acid constituents of petroleum distillates which comprises passing a vapor of a petroleum distillate containing inorganic acidic materials which react with an alkali metal naphthenate to form naphthenic acid into intimate contact, in a neutralizing zone, with an alkali metal naphthenate, with resultant reaction of such inorganic acidic material with the alkali metal naphthenate and the formation of naphthenic acid, withdrawing the vapor so treated, bringing at least a part of the condensate containing the naphthenic acid into intimate contact with an alkali metal hydroxide with resultant regeneration of the alkali metal naphthenate, and returning regenerated alkali metal naphthenate to the neutralizing zone for reaction with more vapors of the petroleum distillate containing the inorganic acidic material.

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