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PROCESS FOR MAKING HEAVY DUTY LIQUID DETERGENT COMPOSITIONS

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U.S. Cl. 252—137 1 Claim

ABSTRACT OF THE DISCLOSURE

Heavy duty liquid detergents in the form of emulsions wherein the organic active is maintained in a dispersed phase, and said dispersed phase is stabilized in a continuous aqueous phase by a polyelectrolyte. The continuous aqueous phase contains a builder combination of sodium tripolyphosphate and potassium nitrilotriacetate.

The present invention relates to a heavy duty liquid laundry detergent composition in the form of an emulsion; more particularly, a phase stable heavy duty liquid laundry detergent composition containing as builders sodium tripolyphosphate, and potassium nitrilotriacetate in a continuous aqueous phase, and containing the surface active agent in the dispersed phase which is stabilized in the aqueous phase by a polyelectrolyte.

Some of the advantages of liquid detergents well known in the art include, for example, freedom from dust and ease of use, particularly, in automatic dispensers and measuring devices found on many present-day washing machines. Since liquid detergents are concentrated, packages containing them take up less space and are easier to handle. Before washing, liquid detergents can be used to treat heavily soiled spots and stains on fabrics.

To be as effective as a conventional heavy duty solid detergent, a liquid detergent must contain an adequate amount of builder, that is, an auxiliary agent used with a surface active agent to improve detergency. Desirable builders are inexpensive and compatible with other components, both organic and inorganic, normally found in detergents. The polyphosphates and pyrophosphates, as is well known, are used as builders in detergent compositions, the most effective member being sodium tripolyphosphate. However, sodium tripolyphosphate is not generally used as a builder in a liquid detergent composition, mainly because of this compound's low solubility in an aqueous solution and its hydrolytic degradation to pyrophosphate and orthophosphate. The pyrophosphates, especially potassium pyrophosphate, have been used as builders in liquid detergent compositions, because, among other things, of their high solubility in an aqueous solution; however, these compounds are not as effective and are more expensive than sodium tripolyphosphate.

When moderate amounts of inorganic or organic builders (and/or other inorganic salts) are used with a nonionic organic surface active agent, the temperature for phase separation is generally lower than room temperature. To prepare a homogeneous product containing an adequate amount of builder, either the nonionic surfactant is dissolved in the builder solution by a solubilizing agent, or the nonionic is allowed to remain as a separate phase, but this separate phase is dispersed and stabilized in the builder solution.

It, therefore, would be an improvement over the art

to provide a liquid detergent composition containing an appreciable amount of sodium tripolyphosphate as a builder. It would be a further improvement over the art to provide a liquid detergent composition in the form of an emulsion which is phase stable and contains a nonionic organic active and an appreciable amount of sodium tripolyphosphate.

It is, therefore, a primary object of this invention to provide a heavy duty liquid laundry detergent composition, in the form of an emulsion, containing a builder combination which imparts improved performance to the composition.

It is another object of this invention to provide a heavy duty liquid laundry detergent composition in the form of an emulsion containing sodium tripolyphosphate and potassium nitrilotriacetate as a builder combination.

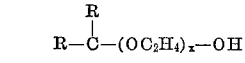
It is another object of this invention to provide a heavy duty liquid laundry detergent composition in the form of an emulsion containing potassium nitrilotriacetate and an appreciable amount of sodium tripolyphosphate as a builder combination.

It is another object of this invention to provide a heavy duty liquid laundry detergent composition in the form of an emulsion which is phase stable containing potassium nitrilotriacetate and an appreciable amount of sodium tripolyphosphate as a builder combination.

Other objects will become apparent from reading the following more detailed description.

The above objects can be accomplished by preparing a heavy duty liquid laundry detergent composition in the form of an emulsion comprising a continuous aqueous phase containing as a builder sodium tripolyphosphate and potassium nitrilotriacetate; a dispersed or internal phase containing as an organic active a nonionic alcohol-ethylene oxide condensate; and containing a polyelectrolyte as an emulsion stabilizer.

The organic actives that can be used in practicing this invention are alcohol-ethylene oxide condensates of the general formula:



where R is selected from the group consisting of an alkyl containing from about 5 to about 20 carbon atoms and hydrogen, when both R's are alkyl the total number of carbon atoms does not exceed about 20; x is a number from about 3 to about 15. Some examples of alcohols which can be condensed with ethylene oxide include: hexane-1-ol, octane-1-ol, decane-1-ol, undecane-1-ol, dodecane-1-ol, tetradecane-1-ol, pentadecane-1-ol, octadecane-1-ol, nonadecane-1-ol, hexane-3-ol, octane-3-ol, dodecane-3-ol, pentadecane-3-ol, nonadecane-3-ol, heptane-6-ol, tridecane-6-ol, hexadecane-6-ol, dodecane-8-ol, tetradecane-10-ol, octadecane-14-ol, 3-methyl hexane-1-ol, 4-methyl decane-1-ol, 8-methyl tetradecane-1-ol, 10-methyl octadecane-1-ol, 5-ethyl heptane-1-ol, 7-ethyl nonadecane-1-ol, 9-ethyl tridecane-1-ol, 11-ethyl heptane-1-ol, 2-methyl hexane-3-ol, 5-methyl decane-5-ol, 7-methyl tetradecane-8-ol, 11-methyl octadecane-14-ol, 6-ethyl octane-4-ol, 9-ethyl pentadecane-12-ol, 11-ethyl octadecane-15-ol, and mixtures thereof.

In practicing this invention, preferred alcohols include dodecane-1-ol, tridecane-1-ol, tetradecane-1-ol, pentadecane-1-ol, and mixtures thereof. The majority of those alcohols listed hereinbefore and used in the novel com-

positions of this invention are biodegradable and are preferred as such. However, it is to be understood that non-biodegradable alcohols can be used if circumstances warrant such a utility.

The number of moles of ethylene oxide condensed with the above alcohols can vary from about 3 moles to about 15 moles, and a preferred range is from about 8 moles to about 12 moles.

The aforementioned alcohols can be used in amounts from about 5% by weight to about 15% by weight of the liquid detergent composition and preferably from about 8% by weight to about 12% by weight. The meaning of the term "liquid detergent composition" as used herein generally connotates a composition containing actives, builders, polyelectrolytes and other non-essential ingredients such as optical brightners, pigment dyes, corrosion inhibitors, perfumes, etc. Consequently, the weight percentages given herein are predicated upon the total weight of such liquid detergent composition.

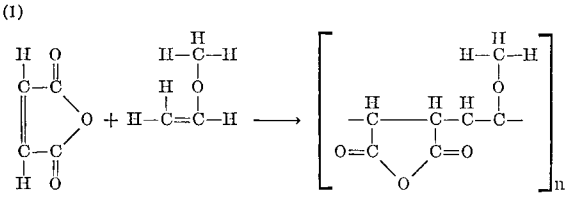
The present invention employs a builder combination of potassium nitrilotriacetate and sodium tripolyphosphate. By using this builder combination an appreciable amount of sodium tripolyphosphate which resists hydrolytic degradation at elevated temperatures can be incorporated into a liquid detergent composition. As shown by the examples hereinafter set forth, the novel compositions of the present invention perform well as heavy duty detergents and are a significant improvement over the prior art detergents.

The exact action which potassium nitrilotriacetate exerts on sodium tripolyphosphate is not known; however, it has been theorized that potassium nitrilotriacetate acts in some manner as a solubilizer for sodium tripolyphosphate. It is to be understood that any theories or ideas set forth herein are merely speculative and are not to be considered limitations on the invention.

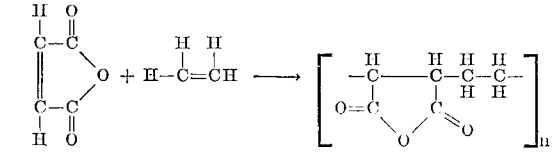
Sodium tripolyphosphate can be used in amounts from about 5% by weight to about 13% by weight of the liquid detergent composition and preferably from about 10% by weight to about 12% by weight. Potassium nitrilotriacetate can be used in amounts from about 5% by weight to about 30% by weight of the liquid detergent composition and preferably from about 10% by weight to about 16% by weight.

The polyelectrolytes that can be used in preparing the present invention include the copolymer of maleic anhydride and ethylene and the copolymer of maleic anhydride and methylvinylether. The specific viscosity of such polyelectrolytes can be determined by using ASTM-D-445-46T Method B; a copy of this procedure may be obtained from United States of America Standards Institute, 10 E. 40th Street, New York, N.Y., 10016. Essentially, this method entails dissolving 1% by weight of the copolymer in 99% by weight of dimethylformamide and subsequently measuring the specific viscosity of the resulting solution at 25° C. using an Ostwall Viscometer. The following reactions illustrate the formation of the respective copolymers:

(1)



(2)



A wide variety of copolymers which impart a low viscosity to the finished product can be used to prepare stable emulsions of the present invention. It is undesirable to prepare a liquid detergent composition having a high viscosity since it will not flow freely from its container and thus would be commercially impractical. Consequently, it is preferred to utilize copolymers which give the final product (i.e. the liquid detergent composition) relatively low viscosities of from about 250 cps. to about 700 cps. at room temperature, i.e. about 20° C. The specific viscosities of the copolymers of maleic anhydride and ethylene which can be used in practicing this invention range from about 0.1 to about 1.2 and of maleic anhydride and methylvinylether range from about 0.5 to about 3.0. These copolymers can be used in amounts from about 0.2% by weight to 2.0% by weight of the liquid detergent composition and preferably from about 0.7% by weight to about 1.1% by weight.

Other ingredients which can be used in the novel compositions of the present invention, in addition to the abovementioned essential components, include compounds such as alkali metal silicates, sodium carboxymethylcellulose, dyes, and fluorescent dyes, etc. The quantities of these other ingredients with the exception of the abovementioned essential components are not critical and persons skilled in the art can determine the proper amounts for their own particular requirements. The quantities of some of these other ingredients include, for example, sodium silicate in amounts from about 3% by weight to about 10% by weight of the liquid detergent composition; sodium carboxymethylcellulose in amounts from about 0.5% by weight to about 4% by weight of the liquid detergent composition; pigment dyes in amounts from about 0.05% by weight to about 0.08% by weight of the liquid detergent composition; and fluorescent dyes from about 0.1% by weight to about 0.8% by weight of the liquid detergent composition.

In practicing the present invention, it is desirable to emulsify the essential ingredients in order that an organic active can be maintained in a concentrated salt solution (usually of inorganic and/or organic builders, corrosion inhibitors, antideposition agents, etc.) without the immediate separation of the organic active. The above process permits the nonionic to remain in a dispersed phase, and the aforementioned copolymer stabilizes the dispersed phase in continuous phase which contains the builder combination.

Generally speaking, the method for preparing the novel compositions of the present invention can be divided, for the sake of clarity, into three distinct steps, namely, (1) hydrolysis, (2) esterification and (3) pH raising.

The hydrolysis step of the present process must be performed while the copolymer is dispersed through (or maintained completely in contact with water therein in some manner) a liquid aqueous medium having a pH below about 6, preferably from about 1 to about 4. In addition, the temperature of the acidic aqueous medium or solution is maintained between about 50° C. and about 85° C. (preferably between about 55° C. and 75° C.) for a period of time which has been found to vary depending upon the specific viscosity of the particular copolymer being employed, for example, the copolymers of maleic anhydride and methylvinylether, have a hydrolysis time that ranges from about 10 minutes to about 50 minutes. At temperatures below 50° C., the necessary type of hydrolysis of the copolymer does not effectively occur, or occurs so slowly as to make any process resulting from use of such low hydrolysis temperatures commercially undesirable. Only partial hydrolysis of the copolymer occurs during this step.

The esterification step of the present invention process involves essentially the intermixing of a quantity or an amount of an organic active that is capable of reacting

with the hydrolyzed "groups" (apparently the free carboxylic acid groups) on the partially hydrolyzed copolymer (resulting from the hydorlysis step described above) to form ester groups. It is desirable that the amount of the organic active used during this esterification step be within the range of from about 5% by weight to about 15% by weight of the liquid detergent composition. It has been observed during the experimentation on the present invention that it is desirable to have more than the amount of reactive surfactant necessary to saturate the aqueous medium during the esterification step. The amount of organic active used is thus preferably within the range of from about 8% by weight to about 12% by weight of the liquid detergent composition during the esterification step. Furthermore, the temperature and the pH of the aqueous medium are variables which are controlled for certain periods of time during the esterification step. More specifically, the temperature is maintained within the range of about 50° C. and about 85° C., preferably between about 55° C. and about 75° C., and the pH of the aqueous medium during esterification is continuously held below about 6, preferably between about 1 and about 4 during such periods of time.

The period of time referred to with respect to the esterification step of the preferred process can vary to some extent, the particular range being primarily determined by the particular copolymer involved, for example, the esterification time of the copolymers of maleic anhydride and methylvinylether ranges from about 10 minutes to about 35 minutes. Only partial esterification of the acidic (partially hydrolyzed) copolymer occurs during the above-described esterification step.

During the pH raising step, the pH of the aqueous medium (containing the partially esterified copolymer organic surface active agent mixture) is raised to at least about 10, thereby preventing any additional acidic hydrolysis or esterification from occurring. Potassium hydroxide in amounts from about 3% by weight to about 12% by weight of the liquid detergent composition is a preferred compound used to raise the pH. Other compounds can be used in conjunction with the potassium hydroxide to and in raising the pH and some of these include, for example, potassium nitrilotriacetate in amounts from 8% by weight to about 15% by weight of the liquid detergent composition, sodium tripolyphosphate in amounts from about 10% by weight to about 13% by weight of the liquid detergent composition, sodium carboxymethylcellulose in amounts from about 1% by weight to about 3% by weight of the liquid detergent composition.

The processes used to prepare the novel compositions of the present invention are disclosed in U.S. Pat. 3,457,176 filed Oct. 16, 1964 and which is assigned to the same assignee of the present invention.

A preferred embodiment of the present invention comprises (1) from about 8% to about 12% by weight of organic actives, such as, dodecane-1-ol, tridecane-1-ol, tetradecane-1-ol, pentadecane-1-ol, etc., (2) from about 10% to about 12% by weight of sodium tripolyphosphate, (3) from about 10% to about 16% by weight of potassium nitrilotriacetate, (4) from about 0.7% to about yde, from about 7% by weight to about 15% by weight of 1.1% by weight of the copolymers of maleic anhydride and ethylene, or the copolymers of maleic anhydride methylvinylether and other non-essential ingredients including, for example, from about 0.01% by weight to about 0.03% by weight of a pigment dye, from about 0.1% by weight to about 0.3% by weight of a fluorescent dye from about 7% by weight to about 15% by weight of potassium hydroxide, from about 0.5% by weight to about 3.0% by weight of sodium carboxymethylcellulose and from about 6% by weight to about 10% by weight of sodium silicate. Liquid detergent compositions containing the above components, have excellent washing abilities and can be used in automatic devices on modern washing machines.

In the following examples, which illustrate some of the preferred embodiments of the present invention, all parts are given by weight percent of the total composition unless otherwise stated.

EXAMPLE I

A novel composition of the present invention was prepared containing the following ingredients:

Material:	Percent
Water [1]	46.3
Pigment dye	0.02
Fluorescent dye	0.20
Methylvinylether maleic anhydride (specific viscosity 1.5–2.0)	0.8
Nitrilotriacetic acid	3.00
Potassium hydroxide (45% by weight)	2.90
C_{12}–C_{15} primary alcohol+9 moles ethylene oxide	10.00
Potassium nitrilotriacetate (51% by weight)	14.10
Sodium tripolyphosphate	12.0
Sodium carboxymethylcellulose (65% by weight)	1.0
Potassium hydroxide (45% by weight)	4.4
Sodium silicate (1:2.4 47% by weight)	7.8

[1] 2.5% excess water added for evaporation.

Into a six blade turbine mixer having a tip speed of 1000 feet per minute were charged the water, which had been preheated to 65° C. and the dyes. The copolymer of maleic anhydride and methylvinylether was slowly added and mixed for about 30 minutes to bring about hydrolysis. Nitrilotriacetic acid and potassium hydroxide were added to form the half salt of potassium nitrilotriacetate. A mixture of (C_{12}–C_{15}) primary alcohols condensed with nine moles of ethylene oxide which had been preheated to 65° C., was gradually added and agitated for about 20 minutes to bring about esterification. Potassium nitrilotriacetate was slowly intermixed keeping the temperature from about 65° C. to about 80° C., then sodium tripolyphosphate. Sodium carboxymethylcellulose, potassium hydroxide and sodium silicate were separately added and mixed for about 15, 2 and 10 minutes, respectively.

The above mixture had a pH of about 11.9 and an initial viscosity of 620 cps. as measured by a Brookfield Viscometer using a No. 3 spindle at 60 r.p.m. for 30 seconds. The viscosity was well within the acceptable range hereinbefore discussed.

The phase stability was determined by a centrifuge test. This test was developed to simulate prolonged storage conditions because of the impracticality of testing detergents under actual conditions. The results of this test have been found to correlate with data taken from actual tests under prolonged storage conditions. The test involves centrifugation of the material in a calibrated glass centrifuge tube. A Clay Adams Centrifuge is used at full speed (1000 gravities) for 60 minutes, at a temperature of about 27° C. Formulations that exhibit less than 6% (by volume) visible separation in this extreme test are considered acceptable and will exhibit excellent stability against phase separations under normal storage and handling conditions, while those that exhibit more than 6% separation are not acceptable. Twelve milliliters of the product of Example I in a calibrated centrifuge tube were centrifuged at a full speed (1000 gravities) in a Clay Adams Centrifuge for one hour. Only 4 volume percent of clear solution was observed at the bottom of the centrifuge tube. Thus, separation in this test was only 4 volume percent, and, therefore, said product is rated acceptable in accordance with the foregoing discussion.

A comparison of the washing performance of the novel composition described in Example I was made with

that of a conventional heavy duty liquid detergent of the following formula:

	Percent
Water	50.92
Dodecyl phenol·10 E.O.[1]	10.00
Brightner dispersion	2.00
Pigment dye solutions	0.02
Methylvinylether maleic anhydride copolymer (specific viscosity 1.5–2.0)	1.00
Tetrapotassium pyrophosphate	25.1
Potassium hydroxide (45% by weight)	1.60
Sodium carboxymethylcellulose (90% by weight)	0.76
Sodium silicate (1:2.35, 43.5% by weight)	8.60

[1] Ethylene oxide.

Data is tabulated in Tables I and II. The testing method utilized is more specifically described in the Journal of the American Oil Chemists Society, Volume 42, pp. 723–727, August 1965, which is hereby incorporated by reference.

TABLE I.—ΔRd GRAYNESS

Temperature 10° C., 50 p.p.m. water hardness

	ΔRd	ΔRd	ΔRd
Concentration, percent	0.15	0.20	0.25
Conventional detergent, percent	10.0	12.2	12.2
Example I, percent	10.8	13.4	12.6

TABLE II.—Δb YELLOWNESS

Temperature 10° C., 50 p.p.m. water hardness

	Δ"b"(—)	Δ"b"(—)	Δ"b"(—)
Concentration, percent	0.15	0.20	0.2
Conventional detergent, percent	0.28	1.08	1.05
Example I, percent	0.68	1.20	1.20

Table I gives the readings taken on a Gardner Color Difference Meter comparing the soil-removing ability of the respective detergents at different concentrations. The higher ΔR*d* reading indicates the better soil-removing ability. As can be seen from Table I, at each respective concentration, Example I exhibits a substantially improved soil-removing ability as contrasted to the conventional liquid detergent.

The ability to decrease fabric yellowness is indicated in Table II by a higher Δ"*b*" reading. As can readily be seen from Table II, the novel composition described in Example I exhibits a superior performance than that of the conventional heavy duty liquid detergent.

The following are typical examples of liquid detergent compositions of the present invention which exhibit superior washing performance were prepared according to the procedure outlined hereinbefore.

EXAMPLE II

	Percent
Water[1]	46.3
Pigment dye	0.07
Fluorescent dye	0.2
Ethylene maleic anhydride (specific viscosity 0.6)	0.8
Nitrilotriacetic acid	3.0
KOH (45% by weight)	2.9
Dodecane-1-ol and Tridecane-1-ol·9 E.O.	10.0
Potassium nitrilotriacetate (51% by weight)	14.1
Sodium tripolyphosphate	5.0
Sodium CMC (65% by weight)	1.0
KOH (45% by weight)	4.4
Sodium silicate (1:2.4, 47% by weight)	7.8

[1] 2.5% excess water added for evaporation.

EXAMPLE III

	Percent
Water[1]	45.2
Pigment dye	0.02
Fluorescent dye	0.20
Methylvinylether maleic anhydride (specific viscosity 1.5+02.0)	0.90
Nitrilotriacetic acid	3.00
KOH (45% by weight)	2.90
4-methyl decane-1-ol·10 E.O.	11.00
Potassium nitrilotriacetate (51.4% solids)	14.1
Sodium tripolyphosphate	12.0
Sodium CMC (65% by weight)	1.0
KOH (45% by weight)	4.4
Sodium silicate (1:2.4, 47% by weight)	7.8

[1] 2.5% excess water added for evaporation.

EXAMPLE IV

	Percent
Water[1]	44.3
Pigment dye	0.02
Fluorescent dye	0.20
Ethylene maleic anhydride copolymer (specific viscosity 0.6)	1.00
Nitrilotriacetic acid	3.00
KOH (45% by weight)	2.90
7-ethyl nonadecane-1-ol·10 E.O.	11.80
Potassium nitrilotriacetate (51% by weight)	14.1
Sodium tripolyphosphate	12.0
Sodium CMC (65% by weight)	1.0
KOH (45% by weight)	4.4
Sodium silicate (1:2.4, 47% by weight)	7.8

[1] 2.5% excess water added for evaporation.

Cross-linked copolymers of ethylene maleic anhydride can be used as stabilizers in the present invention in addition to the linear copolymers of maleic anhydride described hereinbefore. The linear polymers that result from polymerizing maleic anhydride with ethylene can be cross-linked with diamine and alkylene polyamine or a diolefinic material such as an ether or a hydrocarbon etc. Examples of polyamines which have been found to be particularly useful are diethylene triamine, triethylene tetramine, tetraethylene pentamine, and higher molecular weight polyethylene polyamines. Preferred diolefinic cross-linking materials include divinyl benzene, diallyl ether, vinyl crotonate, diallyl esters, and the like.

The solution viscosities of these cross-linked ethylene maleic anhydride copolymers are determined by preparing a 1% solution in distilled water of the cross-linked ethylene maleic anhydride copolymer adjusting the pH to 9 with ammonia and reading the viscosity on a Brookfield LVT Viscometer having a No. 4 spindle and a rotational speed of 6 r.p.m. The temperature is maintained at about 25° C. The cross-linked copolymers of ethylene maleic anhydride that can be used in the present invention have a solution viscosity that varies from about 10,000 cps. to 180,000 cps. For example, 0.8% by weight of ethylene maleic anhydride copolymer cross-linked with vinyl crotonate having a solution viscosity of about 10,000 cps. to about 20,000 cps. can be used to stabilize the detergent active in the continuous aqueous phase.

What is claimed is:

1. A process for producing a heavy duty liquid detergent composition, in the form of an emulsion, said process consisting of:

(A) Charging 46.3 parts by weight of water, 0.02 part by weight of a pigment dye and 0.20 part by weight of a fluorescent dye into a six blade turbine mixer having a tip speed of 1000 feet per minute, said water having been preheated to 65° C.;

(B) Slowly adding a copolymer of maleic anhydride and methylvinylether having a specific viscosity of 1.5 to 2.0 to the mixer and mixing for 30 minutes to bring about hydrolysis;

(C) Adding to the mixer 3.00 parts by weight of nitrilotriacetic acid and 2.90 parts by weight of 45% potassium hydroxide to form the half salt of potassium nitrilotriacetate;

(D) Preheating a mixture of C_{12}–C_{15} primary alcohols condensed with nine moles of ethylene oxide to 65° C., adding this condensation product to the mixer gradually and agitating for 20 minutes to bring about esterification;

(E) Slowly intermixing 14.10 parts by weight of 51% aqueous potassium nitrilotriacetate and 12.0 parts by weight of sodium tripolyphosphate while maintaining the temperature at from about 65° C. to about 80°;

(F) Adding 1.0 part by weight of 65% aqueous sodium carboxymethylcellulose and mixing for 15 minutes;

(G) Adding 4.4 parts by weight of 45% aqueous potassium hydroxide and mixing for 2 minutes; and

(H) Adding 7.8 parts by weight of 47% aqueous sodium silicate and mixing for 10 minutes.

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