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UNITED STATES PATENT OFFICE

2,386,937

UREA PYRIDINIUM COMPOUNDS

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No Drawing. Original application June 23, 1943, Serial No. 492,183, now Patent No. 2,372,257, dated March 27, 1945. Divided and this application April 7, 1944, Serial No. 530,045

7 Claims. (Cl. 260—295)

This invention relates to a new chemical product or compound, our present application being a division of our pending application Serial No. 492,183, filed June 23, 1943, Patent 2,372,257, issued March 27, 1945.

One object of our invention is to provide a new material or composition of matter, that is particularly adapted for use as a demulsifier in the resolution of crude oil emulsions.

Another object of our invention is to provide a novel method for producing said new material or composition of matter.

Briefly described, our new chemical product consists of certain pyridinium compounds containing (*a*) a high molal monocarboxy acyl radical; and (*b*) an urea nucleus. The type of chemical compound herein contemplated, as far as its major aspect is concerned, may be obtained in the following manner: urea, or a substituted urea, and particularly a monoalkyl or dialkyl urea, is treated with an oxyalkylating agent, such as ethylene oxide, so as to introduce at least two hydroxyl radicals, preferably as separate oxyalkylene or polyoxyalkylene radicals. Such polyhydric urea derivative is then esterified with a high molal monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms. The high molal monocarboxy acids may be exemplified by the higher fatty acids. The esterification is conducted so that there is present at least one unesterified hydroxyl radical. Such esterified oxyalkylated urea or oxyalkylated substituted urea, is reacted with one or more moles of a pyridine hydrohalide, such as pyridine hydrochloride, or its equivalent, so as to obtain the new compound or composition of matter herein contemplated. The method of preparation and the structure of the compound will be described subsequently in greater detail.

It is well known that certain pyridinium compounds are obtainable by reactions involving the elimination of a mole of water formed by reaction between a pyridinium hydrogen atom and the hydroxyl of a hydroxyethyl group or the like. (For example, see U. S. Patent No. 2,273,181, dated February 17, 1942, to De Groote & Keiser; and also U. S. Patent No. 2,290,417, dated July 21, 1942, to De Groote and Keiser.)

It is well known that certain monocarboxy organic acids containing 8 carbon atoms or more and not more than 32 carbon atoms, are characterized by the fact that they combine with alkalies to produce soap or soap-like materials. These detergent-forming acids include fatty acids, resin acids, petroleum acids, etc. For the sake of convenience, these acids will be indicated by the formula R.COOH. Certain derivatives of detergent-forming acids react with alkali to produce soap or soap-like materials, and are the obvious equivalent of the unchanged or unmodified detergent-forming acids; for instance, instead of fatty acids, one might employ the chlorinated fatty acids. Instead of the resin acids, one might employ the hydrogenated resin acids. Instead of naphthenic acids, one might employ brominated naphthenic acids, etc.

The fatty acids are of the type commonly referred to as higher fatty acids; and of course, this is also true in regard to derivatives of the kind indicated, insofar that such derivatives are obtained from higher fatty acids. The petroleum acids include not only naturally-occurring naphthenic acids, but also acids obtained by the oxidation of wax, paraffin, etc. Such acids may have as many as 32 carbon atoms. For instance, see U. S. Patent No. 2,242,837, dated May 20, 1941, to Shields.

We have found that by far the most effective demulsifying agents are obtained from unsaturated fatty acids having 18 carbon atoms. Such unsaturated fatty acids include the fatty acids, such as oleic acid, ricinoleic acid, linoleic acid, linolenic acid, etc. One may employ mixed fatty acids, as, for example, the fatty acids obtained from hydrolysis of cottonseed oil, soyabean oil, corn oil, etc. When our new product is intended to be used as a demulsifier, it is preferably obtained from unsaturated fatty acids, and more especially, unsaturated fatty acids, containing a hydroxyl radical, or unsaturated fatty acids which have been subjected to an oxidation.

As to suitable reactants containing a reactive ethylene oxide ring, or the equivalent, reference is made to U. S. Patent No. 2,208,581, dated July 23, 1940, to Hoeffelmann. As typical examples of applicable compounds may be mentioned glycerine epichlorhydrin, glycidealcohol, ethylene oxide, propylene oxide, butene-2-oxide, butene-1-oxide, isobutylene oxide, butadiene oxide, butadiene dioxide, chloroprene oxide, isoprene oxide, decene oxide, styrene oxide, cyclohexylene oxide, cyclopentene oxide, etc.

As to the reaction of ureas or substituted ureas, followed by esterification with a high molal hydroxy acid, reference is made to U. S. Patent No. 2,083,221, dated June 8, 1931, to De Groote. (See also U. S. Patent No. 2,059,273, dated November 3, 1936, to Piggott.) It is to be noted that in light of present knowledge, there is considerable doubt that any free amino hydrogen atoms

remain in presence of treatment with an excess of a reactant containing a reactive ethylene oxide ring. Furthermore, it is to be noted that the aforementioned patents are concerned with materials which are essentially soluble, i. e., water-soluble esterified oxyalkylated ureas or substituted ureas. In the present instance such esters need not be water-soluble, and as a matter of fact, we prefer to use the particular type of reactant which is water-insoluble prior to reaction with pyridine hydrochloride, or its equivalent. In other words, it is our preference that the solubility be obtained at least largely, and preferably, entirely through the introduction of the pyridinium radical or radicals.

Members of the pyridine series suitable as reactants include pyridine, alkylated derivatives of pyridine, particularly alkylated derivatives in which the alkyl radical contains three carbon atoms or less, and especially methylated pyridines, i. e., pyridines in which one, two, or three methyl groups have been substituted in the nucleus, such as picolines, and collidines. Also suitable as reactants are the comparable quinolines and isoquinolines, along with C-methyl homologues thereof. Coal tar bases represent mixtures of suitable heterocyclic materials which may be used as such, or after suitable purification, without separation into the individual components.

As to the reaction of ureas, or substituted ureas, followed by esterification with a high molal hydroxy acid, reference is made to U. S. Patent No. 2,083,221, dated June 8, 1931, to De Groote. (See also U. S. Patent No. 2,059,273.)

OXYALKYLATED UREA DERIVATIVE

Example 1

1 pound mole of urea is reacted with 4 pound moles of ethylene oxide at a temperature of approximately 100° C. for approximately 6 hours, with constant stirring, until all of the ethylene oxide is absorbed. The ethylene oxide need not be added at one time, but may be added intermittently. In such event, the period of reaction may be considerably longer. If desired, one-half of 1% of sodium methylate may be used as a catalyst.

OXYALKYLATED UREA DERIVATIVE

Example 2

The same procedure is followed as in Example 1, preceding, except that the amount of ethylene oxide employed per mole of urea is doubled.

OXYALKYLATED UREA DERIVATIVE

Example 3

The same procedure is followed as in Example 1, preceding, except that the amount of ethylene oxide per mole is tripled.

OXYALKYLATED UREA DERIVATIVE

Example 4

Diamyl urea is prepared from amylene and a cyanate. (See Berichte, 12, 1331 Custer.) Such substituted urea is treated with ethylene oxide in the same manner as Examples 1, 2 and 3, preceding.

OXYALKYLATED UREA DERIVATIVE

Example 5

The same procedure is followed as in the preceding example, except that the corresponding cyclohexyl urea is substituted for diamyl urea.

OXYALKYLATED UREA DERIVATIVE

Example 6

The same procedure is followed as in Example 4, preceding, except that the corresponding benzyl urea is substituted for diamyl urea.

OXYALKYLATED UREA DERIVATIVE

Example 7

The same procedure is followed as in Example 4, preceding, except that the corresponding phenyl urea is substituted for diamyl urea.

OXYALKYLATED UREA DERIVATIVE

Example 8

N-mono-n-butyl urea $C_4H_9HNCONH_2$ is substituted for amyl urea in Example 4, preceding.

OXYALKYLATED UREA DERIVATIVE

Example 9

N,N' - di-n-butyl urea $(C_4H_9)HNCONH(C_4H_9)$ is substituted for amyl urea in Example 4, preceding.

OXYALKYLATED UREA DERIVATIVE

Example 10

N,N-di-n-butyl urea $(C_4H_9)_2NCONH_2$ is substituted for amyl urea in Example 4, preceding.

OXYALKYLATED UREA DERIVATIVE

Example 11

N-mono-n-butyl thiourea $C_4H_9NHCSNH_2$ is substituted for amyl urea in Example 4, preceding.

OXYALKYLATED UREA DERIVATIVE

Example 12

Other alkylene oxides, such as propylene oxide, butylene oxide, or glycidol, are substituted for ethylene oxide in Examples 1 to 11, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 1

Oxyalkylated urea derivatives, as exemplified by Examples 1 to 12, preceding, are esterified with oleic acid in equimolar proportions, to give the desired ester. (See procedure described in aforementioned De Groote Patent No. 2,083,221.)

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 2

Ricinoleic acid is substituted for oleic acid in Example 1, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 3

Stearic acid is substituted for oleic acid in Example 1, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 4

Naphthenic acids derived from Gulf Coast crude petroleum are substituted for oleic acid in Example 1, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 5

Mixed fatty acids derived from soyabean oil are substituted for oleic acid in Example 1, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

Example 6

Linseed oil fatty acids are substituted for oleic acid in Example 1, preceding.

ESTERS OF OXYALKYLATED UREA DERIVATIVES

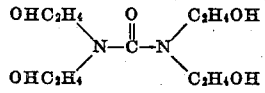
Example 7

In the preceding examples where there are present at least 3 hydroxyl radicals, and preferably, 4 hydroxyl radicals, 2 moles of the fatty acids are employed instead of a single mole.

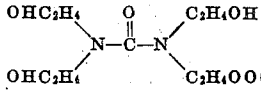
PYRIDINIUM COMPOUND

Example 1

1 mole of urea is treated with 4 moles of ethylene oxide to give tetraethanol urea of the following formula:



Such material is then esterified with a mole of ricinoleic acid indicated by the formula R.COOH, to give the resultant ester of the following composition:

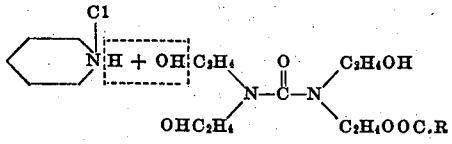


One pound mole of an ester of the kind described immediately preceding is mixed with one pound mole of a hydrochloride of a fraction of pyridine bases (50% distilling, up to 140° C., 90% distilling up to 160° C. completely soluble in water), and one-third pound mole of a mixture of free bases are heated at 100° C., or even higher, for one-half to 5 hours.

Furthermore, at 150 to 160° C. the reaction is more rapid.

Furthermore, pure pyridine may be employed instead of a mixture of the bases. (Compare with Example 2 of Haack Patent No. 2,242,211.) The excess of free pyridine may be removed at the end of the reaction.

Without attempting to specify any specific isomer, but simply by way of illustration, the reaction employed may be indicated as follows:



Example 2

The oxyalkylated urea derived by treating one mole of N-mono-n-butyl urea $C_4H_9HNCONH_2$ with three moles of ethylene oxide is reacted in the same manner as in Example 1, preceding.

Example 3

One pound mole of N,N'-di-n-butyl urea $(C_4H_9)HNCONH(C_4H_9)$ is treated with two pound moles of ethylene oxide and substituted as a reactant in the procedure outlined in Example 1, preceding.

Example 4

One pound mole of N,N-di-n-butyl urea $(C_4H_9)_2NCONH_2$ is treated with 2 pound moles of ethylene oxide and substituted as a reactant in the procedure outlined in Example 1, preceding.

Example 5

The same procedure is followed as in Examples 1 to 4, preceding, except that the amount of ethylene oxide is employed is doubled.

Example 6

The same procedure is followed as in Examples 1 to 4, preceding, except that the amount of ethylene oxide employed is tripled.

Example 7

The same procedure is followed as in Examples 1 to 6, preceding, except that propylene oxide, butylene oxide, or glycide is substituted for ethylene oxide in Examples 1 to 6, preceding.

Example 8

The same procedure is followed as in Example 1, preceding, except that the esterification involves 2 moles of ricinoleic acid for each mole of tetrahydroxyethyl urea.

Example 9

The same procedure is employed as in Example 1, preceding, except that the amount of pyridine hydrochloride per mole of tetrahydroxyethyl urea is doubled.

Example 10

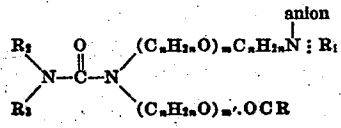
The same procedure is followed in preceding Examples 1 to 9, inclusive, except that one substitutes instead the various esters of oxyalkylated urea derivatives exemplified by Example 1 to 7, preceding, to the extent that they are different from the type already employed in Examples 1 to 9, preceding.

In light of what has been said, it is obvious that the invention may be considered in a somewhat broader aspect. For instance, urea might be treated with two moles of ethylene oxide so as to yield a diethanol urea. Such a product would be perfectly satisfactory as a reactant. The substituted ureas are not necessarily limited to the alkyl type, but as has been suggested previously, any hydrocarbon radical may serve as a substituent for an amino hydrogen atom. In other words, one or more of the amino hydrocarbon atoms, as indicated, may be replaced by an alkyl radical, an aryl radical, an aralkyl radical, or an alicyclic radical. In some instances, such substituted ureas are available by reactions involving primary amines and diethyl carbonate, although unfortunately, the yields are extremely low, even when conducted under pressure, or even when conducted in some other suitable manner. It has been pointed out that the oxyalkylating agent includes glycide and the like. Hereinafter, and particularly in the claims, reference will be made to the alkylene oxides as alkylating agents, and more particularly, in those instances where the number of carbon atoms in the alkylene radical is less than ten, and preferably, not over four. The other variants previously indicated are obvious functional equivalents. Furthermore, the number of times that the ether linkages may occur is not limited, except that obviously there is no need for recurrence beyond the amount necessary to produce a water-soluble ester. However, as previously stated, our preference is that the ester, prior to treatment with pyridine hydrochloride or the like, be water-insoluble. Thus, it is preferred that the recurring ether linkage appear not over ten times. Previous reference has been made to the anion in the form of a halogen ion. Actually, any other suitable salt may ap-

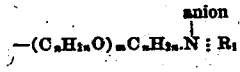
pear as the anion, for instance, a nitric acid radical, an alkyl sulfuric acid radical, a trichloroacetic acid radical, a sulfonic acid radical, etc. In many cases, the most desirable type of material is obtained from a high molal surface-active sulfonic acid acting as the anion. As to the various high molal sulfonic acids which may serve to furnish the anion, reference is made to U. S. Patent No. 2,295,167, dated September 8, 1942, to De Groote & Keiser. Briefly stated, the procedure employed is to neutralize pyridine or the equivalent with a selected sulfonic acid and then react the pyridine hydrosulfonate in the same manner as one would employ a pyridine hydrohalide. Another procedure, of course, simply involves the principle of metathesis. The pyridinium chloride produced in the manner previously described is reacted with the sodium sulfonate in an alcoholic solution, or, in some instances, in an aqueous solution. If the resultant compound, i. e., a compound wherein the anion is the sulfonic acid radical, is water-insoluble, then precipitation takes place in aqueous solution. If, on the other hand, the resultant is water-soluble, then combination takes place in alcoholic solution by precipitation of sodium chloride, which can be removed and the alcoholic solution distilled to eliminate the solvent. Such procedures are described in considerable detail in our co-pending applications Serial Nos. 463,438 and 463,439, both filed October 26, 1942.

It should be noted that the variety of compounds herein contemplated for use as demulsifiers, and for various other uses, may vary from water-insoluble materials to water-soluble materials. They may show various intermediate properties, i. e., some of the compounds may be water-wettable, some may be self-emulsifiable, some may produce cloudy solutions and others may produce clear solutions. Some may show limited solubility in either oil or water.

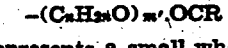
In light of what has been said, the compounds herein contemplated may be represented by the following formula, in conjunction with the obvious equivalents previously referred to:



in which RCO is the acyl radical of a monocarboxy detergent-forming acid having at least 8 and not over 32 carbon atoms; $R_1 \vdots N$ represents a radical derived from a heterocyclic compound consisting of pyridine, quinoline, isoquinoline, and C-methyl linked homologues thereof, and R_2 and R_3 are members of the class consisting of hydrogen atoms, alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals, or either a



radical or a

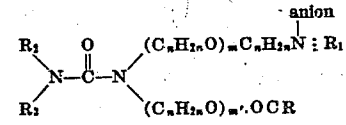


radical; m represents a small whole number not greater than 10, n is a small whole number varying from 2 to 10; and m' represents an integer varying from 0 to 10; R_2 and R_3 may be the same or different. n is preferably 2, 3 or 4. It is obvious that the above formula represents an isomer, whereas, various other isomeric forms may be obtained. Any particular isomer may serve, or a mixture of isomers. For the sake of brevity, in the hereto appended claims the particular formula depicted is intended to include all the various isomeric forms and is not limited to the particular isomer shown. This is true insofar that isomers are all functional equivalents, and are, in fact, metamers. Any other treatment would result in a more involved claim, and perhaps detract from clarity.

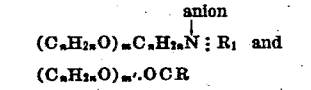
Chemical products or compounds of the kind above described, are adapted to be used as demulsifiers in the resolution of petroleum emulsions of the water-in-oil type; they are adapted to be used in the removal of a residual mud sheath which remains after drilling a well by the rotary method; they may be used as a break inducer in doctor treatment of the kind intended to sweeten gasoline; certain of said products are of value as surface tension depressants in the acidification of calcareous oil-bearing strata by means of a strong mineral acid, such as hydrochloric acid; and some of said products are capable of use as wetting agents in the flooding of exhausted oil-bearing strata, and for various other uses where wetting agents of the conventional type are employed. As to some of such uses which are well known, see "The Expanding Application of Wetting Agents," Chemical Industries, volume 48, page 324 (1941).

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A new chemical product, comprising an urea pyridinium compound of the formula:

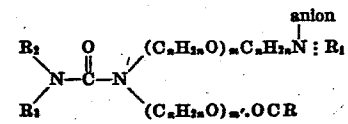


in which RCO is the acyl radical of a monocarboxy detergent-forming acid having at least 8 and not over 32 carbon atoms; $R_1 \vdots N$ is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof; R_2 and R_3 are members of the class consisting of hydrogen atoms, hydrocarbon radicals having less than 8 carbon atoms and selected from the class consisting of alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals, and the radicals



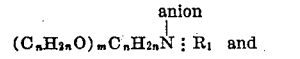
in which m represents a small whole number not greater than 10, n represents a small whole number greater than one and not greater than 10 and m' represents an integer varying from 0 to 10.

2. A new chemical product, comprising an urea pyridinium compound of the formula:



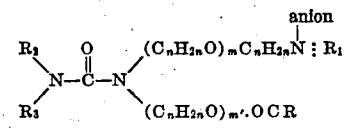
in which RCO is the acyl radical of a higher fatty acid having at least 8 and not over 32 carbon atoms; $R_1 \vdots N$ is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof; R_2 and R_3 are members of the class consisting of hydrogen atoms, hydrocarbon radicals having less than 8 carbon atoms and selected from the class con-

sisting of alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals, and the radicals

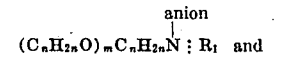


in which m represents a small whole number not greater than 10, n represents a small whole number greater than one and not greater than 10, and m' represents an integer varying from 0 to 10.

3. A new chemical product, comprising an urea pyridinium compound of the formula:

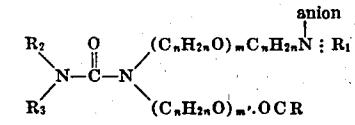


in which RCO is the acyl radical of an unsaturated higher fatty acid having at least 8 and not over 32 carbon atoms; R_1⋮N is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof; R_2 and R_3 are members of the class consisting of hydrogen atoms, alkyl radicals, aryl radicals, aralkyl radicals, hydrocarbon radicals having less than 8 carbon atoms and selected from the class consisting of alicyclic radicals, and the radicals

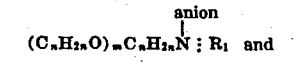


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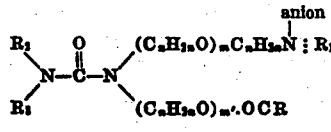


in which RCO is the acyl radical of an unsaturated higher fatty acid having 18 carbon atoms; R_1⋮N is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof: R_2 and R_3 are members of the class consisting of hydrogen atoms, hydrocarbon radicals having less than 8 carbon atoms and selected from the class consisting of alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals, and the radicals

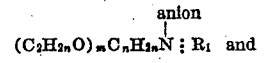


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5. A new chemical product, comprising an urea pyridinium compound of the formula:

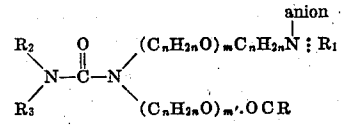


in which RCO is the acyl radical of an unsaturated higher fatty acid having 18 carbon atoms; R_1⋮N is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof; R_2 and R_3 are members of the class consisting of hydrogen atoms, hydrocarbon radicals having less than 8 carbon atoms and selected from the class consisting of alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals, and the radicals

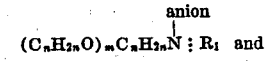


in which m represents a small whole number not greater than 10, n is a small whole number varying from 2 to 10, and m' represents an integer varying from 0 to 10.

6. A new chemical product, comprising a monoquaternary urea pyridinium compound of the formula:

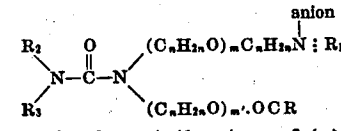


in which RCO is the acyl radical of an unsaturated higher fatty acid having 18 carbon atoms; R_1⋮N is a heterocyclic radical selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals, and C-methyl linked homologues thereof; R_2 and R_3 are members of the class consisting of hydrogen atoms, hydrocarbon radicals having less than 8 carbon atoms and selected from the class consisting of alkyl radicals, aryl radicals, aralkyl radicals, alicyclic radicals; and the radicals



in which m represents a small whole number not greater than 10, n is a small whole number varying from 2 to 10, and m' represents an integer varying from 0 to 10.

7. In the method of manufacturing a urea-pyridinium compound of the formula:



as described in claim 1, the steps of (*a*) hydroxyalkylation of urea involving a reactant having not over 10 carbon atoms; (*b*) esterification of the oxyalkylated urea with a monocarboxy detergent-forming acid having at least 8 and not not over 32 carbon atoms; and (*c*) reaction of the aforementioned ester and a pyridinium salt in which the heterocyclic radical is selected from the class consisting of pyridine radicals, quinoline radicals, isoquinoline radicals and C-methyl linked homologues thereof.

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