Patented Sept. 28, 1943

2,330,524

UNITED STATES PATENT OFFICE

2,330,524

CORROSION INHIBITOR

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No Drawing. Application June 16, 1941, Serial No. 398,337

5 Claims. (Cl. 252—392)

This invention relates to the preparation of compositions of matter adapted for use in the prevention of corrosion of metallic containers used to confine water, alcohols, gasoline or other petroleum distillates including lubricating oils, and the like.

A principal object of the invention is the provision of water-soluble, oil-soluble and alcohol-soluble corrosion inhibitors for protecting, against the agencies of corrosion, metallic containers, composed either of aluminum or aluminum alloys or of aluminum alloys clad with aluminum, which are used for the storage of alcohol, gasoline, oil and the like in airplanes or other transportation equipment which supports its supply of motor fuel for locomotion. Another object of the invention is the provision of water-soluble, oil-soluble and alcohol-soluble compositions for the protection, against corrosive agencies, of iron or steel tanks such as are used for the storage of crude oil, refined oil, petroleum distillates and the like; e. g., where the stored liquids are contaminated with water resulting from the condensation of moisture in the atmosphere above the liquids held in such tanks. Further inventive objects include the provision of corrosion-inhibiting compositions adapted for use in the aqueous cooling systems of internal combustion engines and the like for protecting the latter from corrosion; for the protection against corrosion of auxiliary fuel units and containers proposed for the injection of aqueous alcohols into the combustion chambers of internal combustion engines; and for the protection against corrosion of any aqueous cooling system which is operated at low, ordinary or elevated temperatures.

It has been observed that metallic containers, e. g., such as those composed of aluminum and/or its alloys, iron and/or steel, used generally for the storage of oil, petroleum distillates, lubricating oil, gasoline and the like become damaged by corrosion in relatively short periods of time. The corrosion in such cases is generally confined to the bottoms of such tanks, and is traceable to the corrosive action of water which is found in direct contact with the inner surfaces of the metallic tanks. The presence of water generally is brought about—particularly in partially filled containers—by the condensation of water vapor in the air above the stored liquids; globules of water may be formed on the cool metallic surface when the atmosphere above the liquid reaches dew point temperature, and these globules seek the bottom areas of the containers by gravity difference between the water and the stored liquids. At points of contact between the globules of water and the metallic tank, corrosion takes place, causing pitting, grain boundary corrosion, or other types of corrosion mechanisms, and becomes so pronounced that destruction of containers is caused. This is particularly true in the case of liquids, such as oils, gasoline, distillates and the like, which are non-miscible with water.

It also has been observed that alcohols, e. g., methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl and poly hydroxyl alcohols, glycols, glycol esters, glycerol, and the like, exert a pronounced corrosive action upon metallic containers composed of iron, steel, copper, brass, bronze, aluminum and its alloys, metals plated with dissimilar metals, and the like. In the case of alcohols or like substances which may be employed, either in substantially pure form or diluted with water, as anti-freeze solutions in cooling systems of internal combustion engines, the corrosive action becomes so pronounced that it results in the destruction of the system. The type of corrosion in such cases is of varied mechanisms, the rate of which increases with elevated temperatures, and the resulting products are of such a nature and extent as partially, or completely, to clog the passages of the cooling system, resulting in decreased efficiency and often times complete non-use of the system.

It also has been observed that metallic containers, such as those composed of brass, copper, bronze, aluminum, aluminum alloys, iron, steel and the like, used for the confinement of alcohols (either substantially pure or diluted with water) for auxiliary fuels proposed for use in the operation of internal combustion engines, corrode at a relatively rapid rate at the liquid surface interface contact with such metals. Corrosion also takes place on the submerged surfaces, but not as rapidly, nor does it result in the same pattern as at the liquid line, the corrosion mechanism on the surfaces of the submerged metal differing from that observed at the liquid line, which fact accounts for the different types of corrosion patterns encountered.

It has been observed, also, that surgical instruments, such as those composed of steel, its alloys, plated steel, and non-ferrous metals, corrode when kept in solutions possessing antiseptic properties. Such antiseptic solutions usually consist of a mixture of 85% formalin-alcohol and 15% water approximately. The amount of formaldehyde present usually is found to be 8 to 10% by volume.

It has been observed that mild cold rolled steel of the composition shown for SAE 1020, and steel alloys, when submerged in water corrode in a relatively short period of time. Tools such as agitators, forked instruments, ploughs, cutters and the like composed of iron or steel which are required to operate continuously in contact with water or water soaked mashes, pulps and the like, corrode at a very rapid rate, resulting in

contamination of products and loss of time in replacement of parts destroyed by corrosion.

In the search for suitable soluble corrosion inhibitors it has been discovered that amine salts resulting from the reaction of primary, secondary or tertiary amines of aliphatic, aromatic or cyclic aliphatic hydrocarbons with the saturated carboxylic acids derived from the partial oxidation of hydrocarbons of mineral (e. g., petroleum) origin by the Burwell process (see U. S. Patent No. 1,690,769 to Arthur W. Burwell) are highly effective corrosion inhibitors in solutions of alcohols, glycols, glycol esters, gasoline and other petroleum fractions, including lubricating oils, water and the like. They are highly effective corrosion inhibitors in such media even at relatively low concentrations. For instance, it has been discovered that highly polished specimens of mild cold rolled steel (SAE 1020) do not corrode when submerged in water (either distilled water or water taken from city supply systems) when the latter has been treated with a .1% by volume of an amine salt obtained by reacting primary cyclo hexylamine with carboxylic acids derived from partially oxidized petroleum hydrocarbons. In comparison, steel of the same composition corrodes immediately and rapidly when submerged in untreated water of the same origin. It has also been discovered that steel specimens of mild cold rolled steel do not corrode when submerged in water (either distilled or taken from city supply systems) when treated with .1% to 1.0% of other amine salts obtained by reacting primary, secondary or tertiary amines of aliphatic, aromatic and cyclic hydrocarbons with the aforesaid saturated carboxylic acids derived from partially oxidized hydrocarbons of petroleum origin. It has also been discovered that aluminum, aluminum alloys, iron, and steel do not corrode when submerged in gasoline (or lubricating oil or other petroleum distillate) contaminated with water to which small quantities of the aforesaid amine salts have been added. In comparison, aluminum (or aluminum alloys or iron or steel) submerged in untreated gasoline (or lubricating oil or other petroleum distillate) contaminated with water corrode rapidly (which corrosion begins immediately in the case of iron or steel).

It has been observed that in cases where water has been intentionally added to, and allowed to separate from, the uninhibited gasoline (or distillate or oil) and permitted to deposit on submerged metal, corrosion takes place immediately and eventually becomes so pronounced that it causes pitting at the point of contact between the globules of water and the metal surface. In contrast, metals do not corrode from deposits of water which precipitate from gasoline, petroleum distillates or lubricating oils which contain small amounts of the aforesaid amine salts of carboxylic acids derived from the reaction of aliphatic, aromatic or cyclic amines with saturated carboxylic acids obtained from partially oxidized mineral (e. g., petroleum) hydrocarbons.

When electrical heating units encased in flexible corrodible metal tubes are immersed in water containing .1 to 1.0% by volume of the aforesaid amine salts they do not corrode: in contrast, when immersed in untreated water they corrode rapidly.

It has been discovered that denatured alcohol (composition: 93% specially denatured ethyl alcohol 190° proof, 7% methanol synthetic, known as "Vitol") when diluted with an equal volume of distilled water and treated with .5% by volume of an amine salt made by reacting cyclohexylamine (primary) with the aforesaid saturated carboxylic acids derived from partially oxidized hydrocarbons of petroleum, does not corrode copper, bronze, brass, cold rolled steel (SAE 1020), black iron (hot rolled with mill scale unremoved), or copper with one surface soldered with soft solder, when the metal is suspended, partially immersed, in such a solution. When like metals are suspended, partially immersed, in a non-inhibited solution of the same composition, corrosion products are observed after a few hours on the surfaces of all metals except aluminum alloys: these latter showed evidence of corrosion at the liquid line after several days of exposure to the untreated solution. After several days of such exposure to the untreated solution, at ordinary temperature, all of the metals mentioned showed evidence of cell corrosion which eventually became so pronounced that pitting and grain boundary corrosion resulted.

As will be apparent from the foregoing description, the aforesaid amine salts of "petroleum acids" (by which term are here meant the predominantly saturated, aliphatic, carboxylic acids produced from mineral, e. g., petroleum, hydrocarbons by the Burwell process) are effective as corrosion inhibitors in various types of solutions. It is to be understood that they may be employed with excellent results in any of the common alcohols, glycols, glycol esters and the like or mixture of any two or more of these, in gasoline, lubricating oils and other petroleum distillates, to prevent corrosion of their storage tanks due to water of contamination.

The aforesaid amine salts of petroleum acids are prepared by direct reaction between amines and the petroleum acids. For this purpose, substantially pure petroleum acids (themselves new as compositions of matter) may be employed, or, as will be more fully discussed hereinafter, one may employ semi-purified petroleum acids mixtures containing substantial amounts of non-acidic, difficultly saponifiable or unsaponifiable, bodies which normally are associated with the petroleum acids, per se.

Among operable amine reactants for forming the amine salts are the following:

Alkyl amines

Ethylamine (anhydrous)	Amylamine (mixed isomers)
Diethylamine	Diamylamine (mixed isomers)
Triethylamine	Triamylamine (mixed isomers)
n-Propylamine	n-Amylamine
Di-n-propylamine	Sec-amylamine
Isopropylamine	Sec-hexylamine
Di-isopropylamine	2-ethylbutylamine (hexylamine)
n-Butylamine	n-Heptylamine
Di-n-butylamine	2-ethylhexylamine (octylamine)
Tri-n-butylamine	Dioctylamine (2-ethylhexyl)
Sec-butylamine	
Isobutylamine	
Di-isobutylamine	
n-Butyl diamylamine	

Aryl amines

Diethylbenzylamine	N, N-diamyl aniline (mixed isomers)
N-butyl aniline	p-Tert-amyl aniline
N, N-di-n-butyl aniline	Di-tert-amyl aniline
N-amyl aniline (mixed isomers)	N-n-butyl alpha naphthylamine

Cyclic-paraffinic-amines

Cyclohexylamine	Cyclobutylamine
Di-cyclohexylamine	Di-cyclobutylamine

Substantially pure petroleum acids can be prepared from partially oxidized products resulting from oxidizing mineral (e. g., petroleum)

hydrocarbons under controlled procedures, in the liquid phase, by the Burwell process. For economical purposes, commercially available fractions of petroleum such as, kerosene, 36–40° petroleum distillate, and waxes, are chosen as starting materials for the preparation of oxidized products from which various mixtures of carboxylic acids of different molecular weights and boiling ranges may be obtained. For instance, should it be desired to obtain carboxylic acids ranging in molecular carbon from C_4 through to C_{23}, liquid hydrocarbons ranging in Beaumé gravity from 52° to 36), which hydrocarbons are available in kerosene and 36–40° petroleum distillate fractions, should be chosen as starting materials. On the other hand, should still higher molecular weight carboxylic acids be desired, higher molecular weight, normally solid, hydrocarbons of the waxy type are chosen. Such commercially available waxy type hydrocarbons are known as "sharples wax," crude scale wax, and paraffin wax. Relatively pure carboxylic acids ranging in molecular carbon from C_4 through to C_{33} or higher may be obtained from the oxidation products of such waxes, the major portion of the acidic component of these oxidized products consisting of higher molecular weight acids than those obtained from oxidized normally liquid hydrocarbons. Carboxylic acids can be obtained more economically from the oxidation of normally liquid hydrocarbons such as kerosene or 36–40° petroleum distillate than from the oxidation of higher molecular weight normally solid hydrocarbons such as petroleum waxes.

Amine salts obtained by reacting amines with carboxylic acids derived from the oxidized products of kerosene, fuel oil and petroleum waxes are all effective corrosion inhibitors to a varying degree. Those obtained from reacting amines with the lower molecular weight carboxylic acids obtained from the oxidized products of kerosene, in general are more effective as corrosion inhibitors than those derived from reacting the amines with petroleum acids from the oxidized products of sharples wax or crude scale wax.

The methods and procedures of partially oxidizing kerosene or 36–40° petroleum distillate, and the procedure in the first step of separating saponifiable products from those which do not saponify readily in strong caustic, are given in U. S. Patents Nos. 1,690,768 and 1,690,769 to Arthur W. Burwell. The research disclosed and claimed herein relates in part to the method of recovery of carboxylic acids in substantially pure state from the saponifiable oxygenated products. The soda soaps of the carboxylic acids in the saponifiable mass of the oxidized products of kerosene or 36–40° petroleum distillate are completely hydrolyzed by strong mineral acids (e. g., hydrochloric or sulphuric acid) and the resulting mixture of carboxylic acids, occluded non-acidic oxygenated products and unattacked hydrocarbons is washed with water until free from mineral acids. It has been found that the saponifiable portion of the partially oxidized products of kerosene or 36–40° petroleum distillate when produced on a large scale includes admixtures of such oxygenated products as ketones, alcohols and small amounts of unattacked original hydrocarbons with the carboxylic acids. This mass is then distilled in a stream of relatively dry steam to a final temperature of 550 to 600° F. by application of external heat. Measurement of the temperature is made in the residual mass and not in the vapors. The distillation process is so designed that the current of dry steam is conducted to the bottom of the still and there released so as to pass through the heated mass in order to entrain the volatile products. These volatile products (including water vapor) are condensed and received in a vessel suitable for the separation of the water-insoluble products. The water which contains soluble acids is continually drawn off leaving a light colored distillate of agreeable odor consisting mostly of volatile carboxylic acids, ketones, alcohols, esters, lactones and unattacked hydrocarbons. This distillate is then digested under atmospheric pressure with strong caustic soda (5 normal) for several hours in order completely to saponify the acids and decompose the difficultly decomposable esters and lactones. The unsaponifiable components are then separated from the mixture by diluting the saponified mass with several times its volume of water and keeping the diluted mass warm for several hours. Separation is complete when the subnatant liquid soap layer is no longer clouded with insoluble unsaponifiable compounds. These latter are found in the supernatant layer forming a clear, light colored, agreeable smelling, non-aqueous solution. The aqueous soap solution is drawn off free from the unsaponifiable layer and completely hydrolyzed by strong hydrochloric acid. The so-separated acids are washed sufficiently to remove all traces of mineral acid, and the entrained water permitted to separate by allowing the acids to remain at a slightly elevated temperature for some time. Acids recovered in this manner are clear but usually have a dark wine color. In order to obtain acids of better color, the separated acids are distilled under reduced pressure, resulting in a recovery of about 98 to 99% of relatively light colored pure acids with an agreeable odor.

The neutralization number of acids recovered, by the process just described, from partially oxidized 36–40° petroleum distillate by the Burwell method was found to average 330 (mgs. of KOH per 1 gram of acid). This value was arrived at by averaging a number of results obtained on acids recovered from various lots of oxidized 36–40° petroleum distillate. The distillate was obtained from a given source but oxidized at various times. The extremes of the values were found to be between 310 and 350 (mgs. of KOH per gram of acid). This average neutralization number, namely 330, appears to be typical of this particular group of petroleum acids and may be used as a means of partially identifying them.

It was found that the average saponification number of this group of petroleum acids, after digesting at boiling temperature in strong alcoholic potassium hydroxide was 390 mgs. of KOH per 1 gram of acids. This value is the average of determinations made on a number of recoveries and may be deemed typical of this particular group of petroleum acids. The difference between the neutralization number and the total saponification number of this group denotes the presence, in small amounts, of other saponifiable compounds than the carboxylic groups. These may be esters, lactones, traces of keto-alcohols, or the like.

An average fractional distillation at atmospheric pressure of these petroleum acids was found to be as follows:

	°C.
Initial boiling point	170
Decomposition point	270

Both acid and saponification numbers were determined on equal fractions taken as follows, during the distillation of a certain lot of these petroleum acids:

Fraction No.	Amount	Distillation temperature
	Cc.	
1	20	Distilled between 170° and 210° C.[1]
2	20	Distilled between 210–215° C.
3	20	Distilled between 215–220° C.
4	20	Distilled between 220–224° C.
5	20	Distilled between 224–228° C.
6	20	Distilled between 228–235° C.
7	20	Distilled between 235–241° C.
8	20	Distilled between 241–267° C.
9	25	Distilled between 267–270° C.

[1] Distillate flowed steadily between 200–210° C.

Decomposition (evidenced by incipient evolution of white fumes) started to take place when a temperature reading of 270° C. was reached, and distillation was stopped at this point. The residue (amounting to 1–2% by volume) was found to be a heavy, black tar-like mass.

The neutralization ("acid") and saponification numbers were determined on each of the above fractions and found to be as follows:

Fraction No.	Acid No.	Saponification No.
1	419.6	432.0
2	389.3	
3	381.8	
4	365.2	412.2
5	351.2	401.2
6	332.3	
7	302.2	
8	273.8	341.6
9	227.8	333.3

From the neutralization numbers thus found of the petroleum acids derived from oxidized 36–40° petroleum distillate by the Burwell process, the mean molecular weight of the acids was calculated as follows:

$$M:56.1::1:N$$

hence

$$M=\frac{56.1}{N}$$

M=molecular weight in grams.
N=grams of KOH found to neutralize 1 gram of acid.

The amount of KOH found to neutralize 1 gram of the mixed acids was .033 gram therefore:

$$M=\frac{56.1}{.033}$$

or 170 mean molecular weight. When this mixture of purified petroleum acids was completely reacted with mono-N-amylamine (90% monoamylamine content) it was found that the weight ratio was 1 part acid to .56 part mono-N-amylamine. This reaction is given as follows (where "R" represents the aliphatic radical of the carboxylic acid):

$$R\text{-}COOH+NH_2\text{-}CH_2.(CH_2)_3.CH_3=R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}NH_2.CH_2.(CH_2)_3.CH_3$$

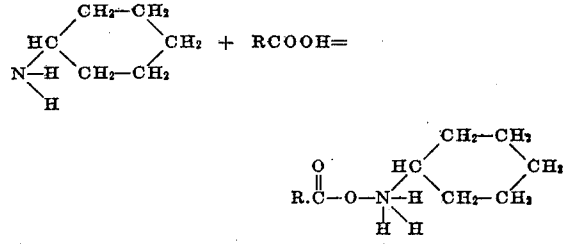
Molecular relation to the mean molecular weight of the petroleum acid is as follows:

87:170=.511

mono-N-amylamine to 1 part petroleum acid.

The actual amount of commercial mono-N-amylamine, 90% content, used completely to react with the acids was found to be .560 part to 1 part of acid. Correcting for the amine content in the commercial product the ratio is 1 part of acid to .504 mono-N-amylamine. This ratio checks very closely with the theoretical; namely, 1 part acid to .511 part mono-N-amylamine which tends to substantiate the mean molecular weight value calculated from the neutralization number.

When commercial N-cyclo-hexyl-amine was reacted to complete neutralization with these petroleum acids, it was found that the combining ratio by weight was 1 part acid to .595 part N-cyclo-hexyl-amine. The cyclo-hexyl - amine content of the commercial product was found to be approximately 95%. This reaction may be exemplified as:



Molecular weight relation to the mean molecular weight of the acids is as follows:

99:170=.582 part N-cyclo hexylamine to 1 part petroleum acid.

It will again be observed that the ratio of commercial N-cyclo hexylamine to petroleum acids agrees very closely to the theoretical ratio, after correcting for the N-cyclo-hexylamine content.

Alkyl, aralkyl, aryl, and cyclo-paraffinic amines react in the same manner with these petroleum acids as described above to form salts. The resulting compounds all possess corrosion-inhibiting properties to a varying degree when used in systems consisting of metal-oil-water. The mono- or primary amine salts of all groups are more potent corrosion inhibitors than are the corresponding salts of either the secondary or tertiary amines, which circumstance may be accounted for by the fact that the primary amine salts are more soluble in the phase of the water-oil systems than the other amine compounds. It has been found that in all groups those petroleum acid salts of amines of hydrocarbon chains containing 5 or more carbon atoms in the chain are more potent corrosion inhibitors than are those derived from amino-compounds having a lower number of carbon atoms. This might be accounted for to some degree on the basis that the lower molecular weight amines are more volatile than those higher in molecular weight, and hence the loss of the inhibitor due to evaporation from the medium in which it is dissolved is greater for the lower molecular weight amine than for that of greater weight. It should be noted, here, that those amine salts from amines containing hydroxyl groups have only a very poor—if any—solubility in gasolines, petroleum distillates, lubricating oils and the like, and hence that such amine salts from hydroxyl amines have only a very limited utility in association with the petroleum products mentioned.

It has also been discovered that the unseparated distillate resulting from the steam distillation, as previously described, of partially oxidized hydrocarbons (kerosene or 36–40° petroleum distillate) when reacted with amines, particularly with mono-amylamine, possesses excellent corrosion-inhibiting properties. This product was found to be very effective in retarding the rate of corrosion of aluminum containers used for the storage of gasoline. It has been observed that containers constructed from a clad metal composed of aluminum over a core of aluminum alloy known as "17ST" corrodes very rapidly in the presence of gasoline containing a small amount of added water. Cup-shaped specimens of this metal (known as "Alclad"), when partially filled with gasoline to which water was added, corroded to such an extent in 20 to 60 days as completely to destroy the container by pitting through the bottom and side walls below the liquid line. The metal walls and bottom in this case were from .35 to .40 inch in thickness. In contrast to this, when the water-containing gasoline was treated with .5% by volume of the amine salt product resulting from the reaction of mono-amylamine with the total steam distillate of the partially oxidized hydrocarbons and placed in the same type of container no corrosion or pitting had taken place during the period of observation. Observation in this case was carried on over a period of 9 months. At the end of this time the inside surfaces of the container were as brilliant as they were at the time the test was started and free from pits and etchings.

It is known that the distillate of oxidized kerosene or 36–40° petroleum distillate recovered by the method previously described, and referred to in the preceding paragraph, consists approximately of 40 to 60% by volume of petroleum acids, and 60 to 40% by volume of unsaponifiable bodies, known to be ketones, alcohols, esters, lactones and unoxidized hydrocarbons. Inclusion of all of these bodies with the amine salts of the petroleum acids—that is to say, use of the mixture referred to in the preceding paragraph—apparently is essential to the long-continued prevention of corrosion of aluminum and aluminum alloys in a system of gasoline-water-metal. Thus, it has been found that when amine salts resulting from the reaction of 2-ethyl-hexyl amine (or mono-amylamine, or mono-cyclohexylamine) with substantially pure petroleum acids was used in gasoline-water mixtures, corrosion of the container—while slowed—did take place, so that at the end of 6 to 7 months storage period destructive corrosion of the aluminum container was evidenced. On the other hand, it was found that when the same volume of unsaponifiable bodies of the steam distillate were used in the gasoline-water mixture no corrosion-inhibiting action was observed: the cup specimen used to confine this mixture corroded in the same period as did those used to confine the untreated gasoline-water mixture. No explanation can be advanced for the peculiar efficacy of the "impure amine salts" product (that is, of the aforesaid mixture of amine salts of petroleum acids with the commonly associated unsaponifiable bodies) as opposed to the pure amine salts alone, and as opposed to the unsaponifiable bodies alone: nevertheless, it is a fact.

I claim:

1. A corrosion-inhibiting composition soluble in mineral oils including gasoline and in normally liquid alcohols of the type of ethyl alcohol, comprising a mixture of organic reaction products of an organic amine having at least 5 carbon atoms per molecule and selected from the group consisting of alkyl amines, cyclo-paraffinic amines and aryl amines, with a mixture of substantially aliphatic saturated carboxylic acids derived from a normally liquid fraction of petroleum by liquid-phase partial oxidation of the latter.

2. The corrosion-inhibiting composition defined in claim 1, in which the organic amine employed in the reaction is primary cyclohexyl amine.

3. The corrosion-inhibiting composition defined in claim 1, in which the organic amine employed in the reaction is mono-N-amylamine.

4. The corrosion-inhibiting composition defined in claim 1, in which the organic amine employed in the reaction is 2-ethyl-hexylamine.

5. The corrosion-inhibiting composition defined in claim 1, in which the mixture of substantially aliphatic saturated carboxylic acids employed in the reaction has a mean molecular weight of about 170.

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