Patented Sept. 28, 1943 2,330,525

UNITED STATES PATENT OFFICE

2,330,525

CORROSION INHIBITOR

James E. Shields, Niagara Falls, N. Y., assignor to Alox Corporation, New York, N. Y., a corporation of New York

No Drawing. Original application June 16, 1941, Serial No. 398,337. Divided and this application September 29, 1941, Serial No. 412,911

5 Claims. (Cl. 260—632.5)

This invention relates to the preparation of compositions of matter adapted for use in the prevention of corrosion of metallic—more particularly, aluminum—containers used to confine water, alcohols, and the like.

A principal object of the invention is the provision of water-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 and the like in airplanes.

It also has been observed that metallic containers, such as those composed of aluminum, aluminum alloys, 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.

In the search for suitable soluble corrosion inhibitors it has been discovered that an esterified product formed by esterifying, with a relatively low molecular weight aliphatic alcohol, the esterifiable constituents of a steam distillate of the reaction mixture obtained by 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, water and the like.

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	341.0
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.

It has been discovered that the products resulting from the esterification, by means of ethyl, propyl, butyl or similar relatively low molecular weight aliphatic alcohol, of the esterifiable components of the steam distillate, above described, from oxidized hydrocarbons of mineral origin (e. g., kerosene, or 36–40° petroleum distillate or the like) are effective as corrosion inhibitors, and particularly so in preventing the corrosive action of aqueous alcohol systems on aluminum alloys. It has been observed that a mixture of 50% denatured alcohol and 50% water (more or less) when stored in aluminum containers, at ordinary temperatures, first blackens the walls of the container in 2 to 3 days and finally begins to etch and pit the surface at this point in 10 to 15 days; at elevated temperatures, the rate of reaction with the metal is greatly accelerated. In contrast, when .5% by volume of steam distillate from oxidized kerosene (or 36–40° petroleum distillate) which has been esterified with n-butyl alcohol is added to a mixture of 50% denatured alcohol and 50% water no corrosion takes place when such a mixture is confined in aluminum containers. The same good corrosion inhibiting effect is had from the use of relatively small amounts (of the order of .5%) of other alkyl esters of other semi-purified, or purified, petroleum acids.

This application is a division of my application Serial No. 398,337, filed June 16, 1941.

I claim:

1. Method of preventing the corrosive action of an aqueous alcohol on an aluminum or aluminum alloy container therefor, which consists in associating with the alcohol in such container a relatively small amount, of the order of 0.5% by weight, of an alcohol-soluble and water-soluble esterified product formed by esterifying with a relatively low molecular weight aliphatic alcohol the esterifiable constituents of a steam distillate of an oxidation reaction mixture produced by subjecting a normally liquid petroleum hydrocarbon mixture to controlled liquid-phase partial oxidation, which esterified product consists essentially of alkyl esters of a mixture of substantially saturated aliphatic carboxylic acids having an average neutralization number of 330, an average saponification number of 390 and a mean molecular weight of 170.

2. Method of preventing the corrosive action of an aqueous alcohol on an aluminum or aluminum alloy container therefor, which consists in associating with the alcohol in such container a relatively small amount, of the order of 0.5% by weight, of an alcohol-soluble and water-soluble corrosion-inhibiting agent consisting predominantly of lower alkyl esters of a mixture of

substantially saturated aliphatic carboxylic acids having an average neutralization number of 330, an average saponification number of 390 and a mean molecular weight of 170, said acids being derived from a normally liquid petroleum fraction by liquid-phase partial oxidation.

3. The method defined in claim 2, in which the alkyl esters are butyl esters.

4. An aqueous alcohol containing a relatively small amount, of the order of 0.5% by weight, of an alcohol-soluble and water-soluble composition consisting predominantly of lower alkyl esters of a mixture of substantially saturated aliphatic carboxylic acids having an average neutralization number of 330, an average saponification number of 390 and a mean molecular weight of 170, said acids being derived from a normally liquid petroleum fraction by liquid-phase partial oxidation.

5. An aqueous alcohol containing a relatively small amount, of the order of 0.5% by weight, of an alcohol-soluble and water-soluble composition consisting predominantly of butyl esters of a mixture of substantially saturated aliphatic carboxylic acids having an average neutralization number of 330, an average saponification number of 390 and a mean molecular weight of 170, said acids being derived from a normally liquid petroleum fraction by liquid-phase partial oxidation.

JAMES E. SHIELDS.