Patented Mar. 29, 1932

1,851,493

UNITED STATES PATENT OFFICE

WILLIAM S. CALCOTT, OF PENNS GROVE, NEW JERSEY, AND FRANK A. McDERMOTT, OF CLAYMONT, DELAWARE, ASSIGNORS, BY DIRECT AND MESNE ASSIGNMENTS, TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

NONCORROSIVE ALCOHOLS

No Drawing. Application filed September 11, 1928. Serial No. 305,318.

This invention relates to the treatment of alcohols with substances capable of rendering the alcohols non-corrosive towards iron tanks, drums, etc., and more particularly to alcohol compositions capable of retaining their non-corrosive properties after dilution with other liquids, particularly water.

It is well known that when commercial denatured alcohol is used for the purpose of lowering the freezing point of the circulating liquid of the cooling systems of internal combustion engines, there is usually a considerable corrosion of the iron portions of the system, as evidenced by the rapid appearance of rust in the circulating liquid. The actual amount of corrosion is usually too slight to seriously affect the engine block casting, but the rust in suspension may be deposited in the tubes or narrow interstices of the radiator, thus decreasing the efficiency of the engine, and eventually more or less blocking circulation. It is also well known that ethyl alcohol, unless extremely pure, and especially the ordinary forms of completely denatured alcohol, is to some extent corrosive, even in the undiluted condition toward iron containers, and is more distinctly so when diluted with water.

Various methods have been proposed to obviate these difficulties. For instance, it has been proposed in British Patent 257,881 to add small amounts of sodium benzoate to alcohol to prevent the corrosive action that is so detrimental, and this substance has been applied in alcohol-containing motor fuels. It has also been proposed in British Patent 269,135 to use soaps for this purpose.

These proposed substances, while they to some extent suppress corrosion in drums, tanks, etc., containing undiluted alcohols, lose their protective action almost completely when the alcohol is diluted with water, for example, when these alcohols are used as anti-freeze compounds in automobile radiators.

It has also been the practice to use products known as "pyridine bases", comprising mostly lutidines, as a denaturant. These compounds have also served to protect iron from corrosion by such alcohol in undiluted condition, but are ineffective when the alcohol is diluted.

An object of our invention is the production of non-corrosive monohydric and other alcohols. A further object of our invention is a non-corrosive alcohol that will retain its non-corrosive properties when diluted. A still further object of our invention is an alcohol that will remain non-corrosive when stored in metal containers and when used in the cooling systems of internal combustion engines.

These objects are accomplished by the addition to the alcohols of organic amino compounds, either of a single type or of two or more types, with or without other non-amino-substances. Although we prefer to use aromatic diamines, particularly meta-toluylene-diamine (1-methyl, 2, 4-diamino-benzene) we may use any one or more of the following compounds: meta-toluylene-diamine, paraphenylene-diamine, phenyl-alpha-naphthylamine, alpha-naphthylamine, beta-naphthylamine, ortho-tolidine, benzidine, betaine, ethylene-diamine, diethyl-amine, hexamethylene-tetramine, or their homologs or isomers. The effects of different compounds within the same class are in general the same in kind, though not necessarily in degree.

As an illustration of one embodiment of our invention we may employ meta-toluylene-diamine in a proportion corresponding to a concentration of from 0.01 to 0.5 grams per 100 ml. of the undiluted alcohol. We may also employ simultaneously therewith other substances, such as alkalin salts, other amino compounds, higher fatty acids, and the like; among such other substances which may be used we mention sodium carbonate, phenyl-alpha-naphthylamine and stearic acid.

It has not been our experience that either phenyl-alpha-naphthylamine or stearic acid alone will entirely prevent the corrosion by the alcohol (except the latter in the form of its alkali salts (soaps)). However, as we have stated in the foregoing, the soaps are useless as protective agents after the alcohol is diluted with water. But, the presence of alkalin salts, phenyl-alpha-naphthylamine,

and of stearic acid have been found to favor protective action of the diamine.

A second and more preferred embodiment of our invention comprises the use of 0.05 to 0.1 gram of meta-toluylene-diamine per 100 ml. of alcohol saturated with sodium carbonate, or from 0.1 to 0.5 grams per 100 ml. of the alcohol of a mixture such as 25 parts stearic acid, 50 parts phenyl-alpha-naphthylamine, 25 parts meta-toluylene-diamine.

Although smaller amounts may be effective when the alcohol is in concentrated form, the larger amounts are essential in order to maintain the anti-corrosive effect in the diluted alcohol.

As a further illustrative embodiment of our invention the following is given:

An iron strip freed of scale and rust, which may be done by grinding on an emery wheel so as to expose the clean metal, is washed with ordinary denatured alcohol, and immersed in a quantity of such alcohol in a clean container, and exposed to room temperature in diffused daylight will exhibit many rust spots within 24 hours, and these increase in number and size for approximately 200 hours, after which further change is relatively slight, except that the alcohol may gradually acquire a yellowish color. We have found that if to the alcohol is added meta-toluylene-diamine in the proportion of 0.05 gram per 100 ml., no rust spots developed during a period of approximately 1,000 hours.

We have also found that the inhibition of corrosion of iron strips may be attained under these conditions (i. e., undiluted alcohol, at room temperature, in diffused light) by the saturation of the alcohol with sodium carbonate, or the addition of any alkalin-reacting salt, such as the acetate, lactate, benzoate, phosphate, borate, etc., of either sodium or potassium. We have also found that similar results may be obtained by the use of 0.25 gram per 1,000 ml. of alcohol, of a mixture of the diamine with stearic acid and phenyl-alpha-naphthylamine.

We have found, however, that when similar tests are made with alcohol which has been diluted with, for example, 150% of its volume of distilled water, the alkalin salts alone fail to prevent the corrosion, the corrosion in this case being rapid and extensive, so that the alcohol quickly becomes filled with suspended rust. On the other hand, we have found that in the presence of the diamine, or the mixture of the diamine with other substances disclosed in the foregoing, with or without alkalin salts such as sodium carbonate, the corrosion will be entirely absent or very slight.

As a further illustrative embodiment of our invention the following non-corrosive composition is given:

200 parts by volume of denatured alcohol were diluted with 300 parts of distilled water, and boiled in a Pyrex glass flask, in which was immersed strips of iron free from scale and rust, for a period of 8 hours, allowed to stand for 16 hours without boiling, again boiled for 4 hours, and then allowed to stand without boiling for 20 hours. At the end of this period of time, all the strips of iron were rusty and the alcoholic liquid contained suspended rust particles. A similar solution was then made up to which was added the mixture

	Parts
Meta-toluylene-diamine	25
Phenyl-alpha-naphthylamine	50
Stearic acid	25

in the proportion of 25 grams of the mixture to 10 liters, and the alcohol was further saturated with sodium carbonate. This solution was boiled intermittently with clean iron strips immersed therein for 3 periods, namely, 8 hours, 8 hours, and 4 hours, with intervening standing periods of 16 hours, 16 hours, and 44 hours respectively. At the end of this time, the strips were darkened but showed no rust, and did not rust on exposure to air for several days, while the liquid, although darkened, contained no suspension of rust.

As a proposed commercial application of this invention, ethyl alcohol, preferably denatured in accordance with Government requirements, would have added to it the mixture above described in the proportion of 25 grams to 10 liters (3.25 ounces per 10 gallons), and the alcohol then saturated with sodium carbonate (about 3 grams per 10 liters, or 0.4 ounces per 10 gallons). One function of the sodium carbonate or other alkaline salts is to prevent the development of color due to oxidation or other reaction of the amino-compounds; it also assists in maintaining optimum conditions for the prevention of corrosion when the alcohol is diluted, by decreasing the hydrogen-ion concentration of the solution.

It has furthermore been found that to these mixtures of alcohol may be added glycerol, ethylene glycol, or other similar anti-freeze compounds without minimizing the protective action of these non-corrosive compounds.

It will be understood that the proportions of the compounds and alcohol given in the foregoing are merely illustrative, and that many apparently widely different embodiments of this invention exist and may be practiced without departing from the spirit of the invention, and that we do not intend to be limited to the specific embodiments thereof except as indicated in the appended claims.

We claim:

1. A composition comprising alcohol and an aromatic diamine.

2. A composition comprising alcohol and meta-toluylene-diamine.

3. A composition comprising alcohol, an aromatic diamine and an alkalin-reacting salt.

4. A composition comprising alcohol, meta-toluylene-diamine and an alkalin-reacting salt.

5. A composition comprising alcohol, an aromatic diamine, and substances having anti-oxidant and anti-corrosive properties.

6. A composition comprising alcohol, a homolog of meta-toluylene-diamine, and substances taken from groups including the amino compounds and the higher fatty acids.

7. A composition comprising alcohol, a homolog of meta-toluylene-diamine, an alkalin-reacting salt, and substances taken from groups including the amino compounds and the higher fatty acids.

8. A composition comprising dilute alcohol and an aromatic diamine.

9. A composition comprising dilute alcohol and meta-toluyene-diamine.

10. A composition comprising dilute alcohol, an aromatic diamine and an alkalin-reacting salt.

11. A composition comprising dilute alcohol, meta-toluylene-diamine and an alkalin-reacting salt.

12. A composition comprising dilute alcohol, an aromatic diamine, and substances having anti-oxidant and anti-corrosive properties.

13. A composition comprising dilute alcohol, an aromatic diamine, and substances taken from groups including the amino compounds and the higher fatty acids.

14. A composition comprising dilute alcohol, an aromatic diamine, an alkalin-reacting salt, and substances taken from groups including the amino compounds and the higher fatty acids.

15. A composition comprising ethyl alcohol and an aromatic diamine.

16. A composition comprising ethyl alcohol, an aromatic diamine and an alkalin-reacting salt.

17. A composition comprising ethyl alcohol and meta-toluylene-diamine.

In testimony whereof we affix our signatures.

WILLIAM S. CALCOTT.
FRANK A. McDERMOTT.