Patented Apr. 7, 1942 2,278,765

UNITED STATES PATENT OFFICE

2,278,765

MANIPULATION OF ACETIC ACID

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No Drawing. Application October 21, 1939, Serial No. 300,559

6 Claims. (Cl. 202—39)

This invention relates to the manipulation of hot acetic acid.

The corrosiveness of acetic acid to the common materials of construction has long been recognized as has the variation of intensity of its corrosive effect under various conditions and circumstances. The corrosiveness of relatively dilute acetic acid at ordinary temperatures does not present a difficult corrosion problem. However, elevated temperatures and concentrations accelerate corrosion and intensify the difficulties. Numerous materials have been tried as materials of construction to resist the effect of such acids. Copper has been employed but is subject to the disadvantage that in the presence of air or other oxidizing influences the copper is readily attacked and it therefore becomes essential to take precautions to exclude air or other oxidizing agents. Furthermore the presence of even an exceedingly small quantity of copper in the acid discolors the acid and renders it objectionable to many users. Aluminum is rapidly attacked by acetic acid in concentrations approaching 100%. Tantalum is resistant to attack by acetic acid but is itself too expensive for use in constructing most chemical equipment. Its use as plating or lining for apparatus is hindered by its properties which render special methods of treatment necessary; hence, even employed as a lining material, it is overly expensive. Chromium steels and chromium nickel steels have been found to be fairly satisfactory, but even these alloys are not as resistant as could be desired. This is particularly true in the case of hot acetic acid of concentrations above 99.9%.

I have now found that if a chromium-iron alloy contains a small percentage of molybdenum the resistance of the alloy to corrosion by hot concentrated acetic acid is greatly improved. Thus the presence of about 3% of molybdenum in such an alloy has been found to result in an increase of as much as 7000% in the resistance of the metal to corrosion and in the consequent life of equipment used for handling acetic acid at high temperatures and concentrations, depending upon the particular conditions.

While it has long been recognized that molybdenum may impart valuable properties to iron or steels, the known properties which it is capable of imparting or improving have reference to certain specific uses of the material. Thus, according to Mellor's "Treatise on Inorganic and Theoretical Chemistry" (1931), the molybdenum steels are known to have a "higher elastic limit, and elastic ratio; a higher elongation or greater ductility; and a higher reduction of area or greater toughness." Such properties render the steels particularly suitable for use in the manufacture of motor car frames, shafts and rods, high pressure boiler-plates, linings for big guns, rifle barrels, armor plate and armor-projectiles, steel balls for grinding mills, permanent magnets, etc. In chemical equipment for the manipulation of acetic acid, none of these recognized properties of the molybdenum alloys is necessary in greater degree than supplied by ordinary alloys and as far as I am aware the use of alloys containing molybdenum has never heretofore been proposed for this purpose.

Stated generally, my invention consists in the manipulation of hot concentrated acetic acid in equipment such as vessels, stills, and the like having the surfaces exposed to the hot acid composed of or comprising a chromium-iron alloy containing a small percentage of molybdenum.

For the purposes of the present invention I have found iron alloys containing between 15% and 30% of chromium, and between 1% and 5% of molybdenum to be highly satisfactory. Such alloys are more resistant to corrosion in many cases than corresponding alloys containing much higher proportions of chromium but without the molybdenum.

My invention contemplates the storage, conveyance, or chemical or physical treatment of hot concentrated acetic acid including the anhydrous acid in contact with surfaces such as containers, pipes, agitators and auxiliary equipment of a chromium iron containing a small proportion of molybdenum and is particularly concerned with the distillation of acetic acid of at least 50% concentration to separate it from impurities and produce vapors of anhydrous acid at elevated temperatures, in distillation equipment composed of an alloy comprising between 16% and 20% chromium, between 6% and 14% nickel, and between 2% and 4% molybdenum.

The astonishing properties of the molybdenum-containing alloys will be apparent from the results of comparative tests of two illustrative materials.

An iron alloy containing 18.4% chromium and 9.3% nickel, was compared with a similar alloy containing 17.8% chromium, 9.3% nickel, and, in addition, 3.4% of molybdenum. The latter alloy was found to have in the neighborhood of 70 times the life of the former in contact with liquid 99.9% acetic acid at 120° C. At 145° C.

its life was four times that of the chromium-nickel alloy. Vapors of 99.9% acetic acid (.1% H_2O) attacked the chromium-nickel alloy 30 times as rapidly at 120° C. and 2⅔ times as rapidly at 145° C.

The comparative lives of the two alloys in contact with hot anhydrous acetic acid likewise was vastly in favor of the molybdenum alloy. For example, hot anhydrous acetic acid vapor attacked the ordinary chromium-nickel-iron alloy twice as rapidly as it attacked the molybdenum-containing alloy. In contact with liquid anhydrous acetic acid the latter alloy had from six to over eight times the life of the former as the temperature varied from 145° C. to 120° C. The rapid attack of the metals by liquid anhydrous acetic acid at temperatures in the neighborhood of 145° C. may be appreciated from the fact that the acid attacks a sheet of ordinary 18–8 alloy sufficiently rapidly to corrode completely through a .06 inch plate in substantially less than a year. The usable life of such a sheet of the 18.4% chromium 9.3% nickel alloy discussed above would be at an end within a year since it would be corroded about 5% of the way through in this time, assuming that only one side of the metal were exposed to attack. On the other hand at least a 5-year life may reasonably be obtained from the 17.8% chromium, 9.3% nickel, 3.4% molybdenum alloy under like conditions.

Although a large increase in corrosiveness is shown as the temperature is increased above 120° C., little difference in corrosiveness is noticeable as the temperature is decreased to 100° C.

I have found that acetic acid of concentration as low as 50% exhibits a behavior practically the same as that of the 99.9% acid. Below 50%, however, for instance at a concentration of 37%, the difference in resistance to corrosion tends to disappear between the alloys containing molybdenum and those which do not contain it and since there is little corrosion of either, either may be employed for handling the acid. On the other hand the effects of acids of more than 99.9% change rapidly, the corrosive effect increasing as the concentration approaches 100%. Thus the life of a chromium-iron alloy in contact with anhydrous acid has been found to be as short as 1/30 and usually from ¼ to ½ that of the same alloy in contact with 99.9% acetic acid. The corrosion resistance of the material in contact with the acid at concentrations above 99.9% thus becomes of increasing importance as the concentration approaches 100%.

I claim:

1. In the manipulation of hot concentrated acetic acid, the improvement which comprises effecting such manipulation by apparatus having its surfaces in contact with the hot acetic acid composed of a chromium-nickel-iron alloy containing between 15% and 30% of chromium, between 6% and 14% of nickel, and between 1% and 5% of molybdenum.

2. In the distillation of acetic acid, the improvement which comprises heating the acetic acid so as to produce vapors of substantially anhydrous acetic acid in a still whose surfaces in contact with the substantially anhydrous acetic acid in liquid and vapor phases are composed of a chromium-nickel-iron alloy containing between 15% and 30% of chromium, between 6% and 14% of nickel, and between 1% and 5% of molybdenum.

3. In the distillation of acetic acid, the improvement which comprises heating the acetic acid so as to produce vapors of substantially anhydrous acetic acid in a still whose surfaces in contact with the substantially anhydrous acetic acid in liquid and vapor phases are composed of a chromium-nickel-iron alloy comprising between 16% and 20% chromium, between 6% and 14% nickel, and between 2% and 4% molybdenum.

4. The method of heating concentrated acetic acid at temperatures of 100° C. and above, which comprises bringing the acetic acid into contact with hot metallic surfaces consisting of a chromium-nickel-iron alloy containing between 16% and 20% chromium, between 6% and 14% nickel, and between 2% and 4% molybdenum.

5. In the manipulation of hot concentrated acetic acid, the improvement which comprises effecting such manipulation by apparatus having its surfaces in contact with the hot acetic acid composed of a chromium-nickel-iron alloy containing between 16% and 20% chromium, between 6% and 14% nickel, and between 2% and 4% molybdenum.

6. In the processing of hot concentrated acetic acid, the improvement which comprises confining the hot acid by metal surfaces composed of a chromium-nickel-iron alloy containing between 15% and 30% of chromium, between 6% and 14% of nickel, and between 1% and 5% of molybdenum.

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