PERFORMANCE OF DOUBLE DISTILLATION IN PURIFYING LIQUID AMMONIA FOR USE IN THERMAL TUBES

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UDC 66.048:541.171.
1/4:536.248.2

A study has been made on the effect of single and double distillation of liquid ammonia on the contents of impurities unfavorably influencing the viability of aluminum-alloy thermal tubes.

Specifications for the working life and reliability of thermal tubes TT are steadily tightening, as well as for systems containing them, so great importance attaches to compatibility of the materials. One of the most effective liquids for use in the range from −60 to 60°C is ammonia. In addition to stainless steel and titanium, this is most compatible with aluminum alloys, which are widely used in current designs [1, 2]. The reactions of liquid ammonia with aluminum alloys are accompanied by slight uniform corrosion, mainly of point character [3, 4], but if this is progressive, it can lead to the TT failing. The initiation and growth of point corrosion are substantially affected by impurities such as water, oxygen, and chlorine.

The equilibrium in the presence of water is

$$NH_3 + H_2O \rightleftarrows NH_3 \cdot H_2O \rightleftarrows NH_4^+ + OH^-. \qquad (1)$$

The aluminum reacts after the protective oxide film has been removed by the NH_4OH solution:

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2 + H_2O, \qquad (2)$$

$$2Al + 6H^+(\text{from water}) \rightarrow 2Al^{3+} + H_2\uparrow, \qquad (3)$$

$$2Al^{3+} + 6OH^- \rightarrow Al_2O_3 + 3H_2O. \qquad (4)$$

In the presence of oxygen, the oxide is formed as follows:

$$2Al + \frac{3}{2}O_2 + x\,H_2O \rightarrow Al_2O_3x\,H_2O. \qquad (5)$$

However, about 10^{-4} vol. % oxygen in the presence of 0.01% water is sufficient [5] to initiate corrosion, which cannot be explained by (5) alone. It is likely that the water hydrates the ammonia and acts as a source of hydroxyl ions, while the oxygen and the chloride or the water and the chloride produce the point corrosion by causing areas on the surface to be in the passive and active states, i.e., oxygen and water are passivators while chloride is an activator [6]. The simultaneous presence of trace amounts of passivators and activators is sufficient for point corrosion to occur. Chromatographic analysis [7] shows that the oxygen level in liquid ammonia is $2 \cdot 10^{-5}$ vol. %, i.e., below the concentration required for corrosion.

As regards water and chloride, the concentrations of these affect the corrosion rate, which means that the ammonia must be purified, particularly from these. One of the simplest ways of removing water and chloride from liquid ammonia is to distill it. To evaluate the performance, we have examine the effects of single and double distillation on the impurity contents.

Figure 1 shows an apparatus for testing TT as widely used during manufacture.

The following sequence was used: 1) determining the impurities in the initial ammonia; 2) determining them after purification; and 3) the same after double distillation.

All-Union Electromechanics Research Institute, Istra. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 3, pp. 415-417, September, 1986. Original article submitted June 28, 1985.

0022-0841/86/5103-1050$12.50

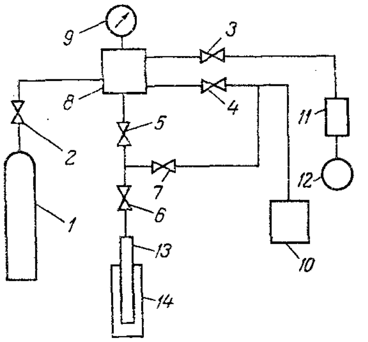

Fig. 1. Apparatus for testing thermal tubes: 1) ammonia cylinder; 2-7) valves; 8) calibrated inlet vessel; 9) vacuum gauge; 10) VIT-1 vacuum meter; 11) nitrogen trap; 12) vacuum pump; 13) thermal tube; 14) vessel containing liquid nitrogen.

TABLE 1. Impurity Contents in Ammonia

Ammonia	Mass fraction of water, %	Mass chloride concn., mg/kg	Mass concn., mg/dm^3	
			iron	oil
Initial	0,027—0,042	0,5—1,15	0,24—0,7	4,5—10,0
After distillation	0,002—0,008	0,1—0,13	0,19—0,3	1,1—2,0
After double distillation	0,001—0,003	Not found	0,1—0,2	2,2—2,8

The initial material was technical liquid ammonia grade A in accordance with GOST 6221-82, where the impurity contents meet the following specifications:

mass fraction of water, %	0.04
mass concentration of total chlorine, mg/kg	–
mass concentration of iron, mg/dm^3	1
mass concentration of oil, mg/dm^3	2

Samples of the initial ammonia were taken in accordance with GOST 6221-82 into a glass sampler of capacity 250 cm^3 in lots of 100-110 cm^3 with obligatory weight testing.

The samples after distillation of double distillation were taken with the TT filling system into a glass sampler of capacity 250 cm^3; the sampler was filled by connecting it to valve 6 in the sequence usually employed in filling TT, i.e., by condensing the gaseous ammonia into the sampler immersed in liquid nitrogen. The sample weighed about 70 g and was checked by weighing with an error of 0.02 g.

The mass fraction of water was determined by electrometric titration with Fischer's reagent, while the mass fraction of iron was determined by photocolorimetry and that of oil by infrared spectroscopy. The methods of determining these impurities are given in GOST 6221-82. the mass fraction of chloride was determined by potentiometric titration with silver nitrate solution. The results were averaged over two parallel determinations.

The following conclusions are drawn from the results (Table 1).

1. The water content can be reduced to 0.001% by double distillation. The large spread in the analyses is due to inadequate measures to prevent contact between the sampled ammonia and the air during the measurements, which leads to the ammonia taking up water vapor from the atmosphere. Many foreign firms restrict water in ammonia to 0.001% or less when it is used in aluminum TT and indicate that contact with air is impermissible during TT filling [1].

2. No chloride was found in the double-distilled ammonia, which shows that the method is very effective.

3. The mass fraction of iron is reduced by about a factor 2.5.

4. This TT filling apparatus contaminates the ammonia with oil, because an oil fore-vacuum pump is used and the measures to freeze out the oil vapor are inadequate.

LITERATURE CITED

1. P. D. Dan and D. A. Ray, thermal Tubes [Russian translation], Moscow (1979).
2. S. Chi, Thermal Tubes: Theory and Practice [Russian translation], Moscow (1981).
3. A. E. Missan, Trudy GIPKh, No. 44, 112-120 (1960).
4. I. F. Nefedova, Trudy GIAP, No. 1, 235-245 (1953).
5. A. D. Hunt, Analyst, 102, 846-851 (1977).
6. Short Chemical Encyclopedia [in Russian], Vol. 2, Moscow (1963), p. 726.
7. G. S. Beskova, M. G. Mamakina, and A. I. Butusova, Zavod. Lab., No. 3, 23-26 (1983).

SONOLUMINESCENCE AND SUBHARMONIC GENERATION IN A CAVITATION ZONE OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

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UDC 534.29:535.37

The variation of the sonoluminescence and the subharmonic component of the cavitation noise spectrum is investigated in a solution of sodium chloride in water.

The investigation of the acoustical and optical characteristics (sound absorption, generation of a characteristic subharmonic frequency of cavitation noise, and the generation of optical luminescence) of a cavitation zone in aqueous solutions of sodium chloride is of considerable interest from two points of view.

First, cavitation exerts a more intense destructive action on metals in aqueous salt solutions, sea water in particular, than in tap or distilled water. This fact has been attributed until now to chemical corrosion, which intensifies cavitation percussion effects [1-3]. Such an explanation has been deemed well justified, especially insofar as chemical reactions, in turn, are strongly intensified in a cavitation zone. However, with an increase in the salt concentration the physicochemical properties of the water change, and this can not only affect the chemical activity of the solutions, but also exert a direct influence on the properties of the cavitation zone has been disregarded to data, and the results of cavitation tests on pure water (e.g., in water tunnels) have been used without any kind of corrections for engineering calculations of systems operating in solutions, specifically in sea water [4].

Second, the physicochemical properties of aqueous sodium chloride solutions have been quite thoroughly investigated. This means that the results of studies of such solutions can be used to assess the influence of the properties of the liquid on the cavitation zone. Moreover, NaCl solutions from the basis of a number of industrial compositions used in ultrasonic industrial processes.

In light of the foregoing considerations, we now report an investigation of the influence of the solution of salt (NaCl) in water on the characteristics of a cavitation zone, viz.: the intensity I_Σ of the total acoustic signal sensed by a hydrophone placed in the cavitation zone, the intensity I_{sub} of the subharmonic component of the total signal, and the sonoluminescence intensity L. We note that the simultaneous investigation of subharmonic generation and sonoluminescence is also of major interest from the standpoint of ascertaining the mechanism of sonoluminescence.

EXPERIMENTAL APPARATUS

A block diagram of the apparatus is shown in Fig. 1. As in [5], we used a pulsed cavitation-generation technique. The pulse-modulated acoustic signal (with a carrier frequency of 0.7 MHz) was excited by means of a focusing piezoelectric ceramic radiator. The use of a

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Institute of Applied Physics, Academy of Sciences of the Belorussian SSR, Minsk. Università di Trieste, Italy. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 3, pp. 417-424, September, 1986. Original article submitted May 27, 1985.

0022-0841/86/5103-1052$12.50