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Review of Aging and Corrosion of Aircraft Integral Fuel Tank Sealing Materials

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Abstract: Polysulfide sealant has excellent oil resistance, water resistance, acid and alkali resistance properties, and thus is widely used as sealing material for fuel tank of aircraft integral structure. Aviation kerosene is easy to produce peroxides under hot oxygen conditions. At the same time, due to improper use and maintenance methods, the kerosene is easy to breed microorganisms, which causes aging and corrosion problems of the sealing rubber layer in the fuel tank to varying degrees, seriously affecting aircraft flight and use safety. In view of the increasingly prominent aging and corrosion problems of sealing adhesive layers in integral fuel tanks, the main issues regarding aging and microbial corrosion mechanisms are summarized, with an emphasis on the anti-aging measures, aging life calculation methods and corrosion protection measures that are responsible for sealing properties. The hot oxygen aging of polysulfide sealant in aviation kerosene leads to a significant decrease in the strength and elasticity of the sealant layer. Although the aging problem of polysulfide sealant cannot be prevented, it can be improved by adding fillers or modifying the polysulfide sealant. The problem of microbial corrosion can be effectively solved by controlling fuel quality, cleaning the fuel tank, sterilizing the fuel tank and other measures.

Keywords: Integral Fuel Tank, Polysulfide Sealant, Aging, Microbial Corrosion

1. Introduction

The aircraft integral fuel tank greatly increased the fuel tank volume as well as the fuel carrying capacity and thus is widely used in modern civil and military aircraft. The realization of sealing performance depends on the sealant in the aircraft fuel tank. In the general service life of aircraft for 20 years, with the increase in flight time, aging corrosion of the sealing layer in the fuel tank intensifies, which seriously affects the sealing performance of the fuel tank and brings great challenges to the maintenance of the aircraft.

The design service life of the aircraft is generally approximately 20 years. However, with the increase in the aircraft's service life, the sealing adhesive layer in the fuel tank exhibits aging corrosion to varying degrees, which seriously affects the sealing performance of the fuel tank of the overall structure and brings great challenges to aircraft safety. Therefore, the key developments and future challenges in this field are summarized. The main issues regarding sealant materials for aircraft integral fuel tanks and their development, the recent progress in the aging mechanism and service life calculation of sealants, and the corresponding corrosion mechanism and protection requirements provide references for the use and repair of sealant materials.

2. Aircraft Integral Fuel Tank Sealing Material

2.1. Introduction of Sealing Materials for Aircraft Integral Fuel Tank

To meet various extreme environments of aircraft during flight, integral fuel tank sealants should satisfy certain requirements for process performance, physical and mechanical properties, environmental resistance, etc. [1]. The polysulfide sealant combines a low molecular weight liquid polysulfide polymer with a thiol end group as the main material, together with an amorphous elastic sealing material prepared by a vulcanizing agent. Excellent comprehensive performance is achieved due to the significant compounding effect. Specifically, the performance of oil resistance, water resistance, acid and alkali resistance, chemical medium resistance, atmospheric aging heat resistance, etc. Thus, it has been widely used for sealing aircraft fuel tanks [2, 3].

Polysulfide sealant is generally composed of base paste and vulcanizing paste and thus be defined as a two-component sealant. The ratio, preparation and curing process of the polysulfide sealant have a crucial influence on the final performance of the polysulfide sealant [4]. Liquid polysulfide rubber is usually obtained by polycondensation reaction of dichloroethyl acetal with sodium polysulfide, and the corresponding formula is shown below:

$$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}S\text{–}S)n\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH \quad (1)$$

That is, the S–S bond in the main structure of the molecule, and the thiol group at the end of the branched chain, which has a significant impact on the molecular weight and cross-linking rate. There are sulfur atoms on the main chain of the liquid polysulfide rubber polymer, and the corresponding C-S and S–S bonds generated by the chemical reaction saturate the molecular chains. Due to the polymer structure above, polysulfide sealants can be used in a wide range of engineering temperatures and provide reliable bonding performance for different material surfaces, such as different metal materials, primer or finish paint and organic glass. At the same time, polysulfide sealants have good resistance to fuel, fuel vapor, water vapor, nonpolar liquid media and atmospheric environments [5, 6].

2.2. Development of Sealing Materials for Aircraft Integral Fuel Tanks

Morton Company first prepared commercial liquid polysulfide rubber [7] through the reaction of dihydroxyethyl acetal and sodium polysulfide. The corresponding polysulfide sealant has excellent oil resistance, corrosion resistance, low temperature resistance, low air permeability and thus be successfully applied to the overall fuel tank sealing of aircraft [8, 9]. Since then, more work focused on the modification of polysulfide rubber, such as toughening modification of polysulfide rubber with epoxy resin or polyurethane resin [10, 11]. The main products include PR series sealant produced by PPG Aviation Materials Co., Ltd., AC series sealant produced by AC Teck Aviation Materials Co., Ltd., MC series sealant produced by Chemetall Aviation Materials Co., Ltd., and CS series sealant produced by Flamemaster. A large number of material standards and process standards are correspondingly proposed, represented by American aerospace material standards, such as AMS3276 and AMS3281 [12, 13] as well as Boeing's material standard BMS5-142 and Airbus's material standard AIMS-04-05-012 [14, 15].

After nearly 50 years of development, China's domestic aviation sealant materials have made great progress. The research on sealant materials has changed from studying the Soviet material system in the 1970s to referring to the advanced technologies of the United States and Europe in the 1980s and then developing sealant materials with complete varieties, stable performance, strong reliability and applicability. After decades of application by the air force and civil aviation, domestic sealant materials meet the requirements of the current military and aircraft. In terms of polysulfide sealant product development, research on polysulfide rubber modification, polysulfide rubber regeneration, adhesive systems and filler system improvement has been carried out, and various products have been developed [16-18]. After years of research and development, the Beijing Institute of Aeronautical Material has developed many generations of sealants with various brands. From XM series to HM series, the performance was improved, and the types were refined. However, most of the products are designed for specific use. There is little research on basic sealing research, sealant supporting products and construction tools.

3. Aging Problem of Sealants for Integral Fuel Tanks

3.1. Study on the Aging Mechanism and Antiaging Performance of Sealants for Integral Fuel Tanks

In view of the serious aging problem of polysulfide sealant in aviation kerosene, Wu et al. [19] studied the aging behavior of polysulfide sealant in aviation kerosene. The chemical change of aviation kerosene in high temperature atmosphere and its impact on polysulfide sealant through performance testing, chemical analysis and instrument analysis. The mechanism of polysulfide sealant aging in aviation kerosene is analyzed, indicating that the strength and elasticity of the polysulfide sealant decreased significantly after aging in aviation kerosene and was accompanied by a significant weight loss, which is attributed to the coupling effect of heat and oxygen. Specifically, aviation kerosene is first oxidized by oxygen in air under high temperature, producing a large amount of peroxides. Aviation kerosene expands the polysulfide sealant at high temperature, and the oxygen absorption efficiency is greatly improved, thus intensifying the thermal oxygen aging process of degradation and cross-linking.

Jet fuel can be oxidized at high temperature or during long-term storage to produce peroxide, which is shown in equation (2). The curve of peroxide value changing with temperature is exhibited in Figure 1. The peroxide is unstable and easily decomposes, which is shown in equation (3).

$$RH+O_2 \rightarrow ROOH \tag{2}$$

$$ROOH \rightarrow RO^* + HO^* \tag{3}$$

The transfer reaction between the free radicals in jet fuel and the polymer chain in the polysulfide sealant causes polymer chain destruction, which is shown in equation (4). At the same time, polysulfide sealant can produce free radicals due to oxidation. The combination of the above two factors led to the serious breakdown of the molecular chain.

$$RO^*+R'\text{-}R'' \rightarrow R'\text{-}OR+R''^*$$

$$HO^*+R'\text{-}R'' \rightarrow R'\text{-}OH+R''^* \tag{4}$$

The molecular chain of the polysulfide sealant possesses a special polysulfide bond structure, which makes it resistant to oil and medium. However, the polysulfide bond structure easily fractures under oxygen conditions with high temperature, which reduces the high-temperature resistance and aging resistance of the polysulfide sealant. The tensile strength and elongation at break decreased at the same time, accompanied by a significant weight loss, indicating that the aging of the polysulfide sealant in jet fuel satisfies the thermal oxidation mechanism.

Li et al. [20] took the liquid polysulfide sealant LP-32 as the research object, and the influence of base paste content and accelerator diphenylguanidine content on the aging performance of polysulfide sealant were discussed. After 7 days of accelerated aging at 100°C, the tensile strength and elongation at break of the aged sealant were much higher than those before aging. Pan et al. [21] studied the air resistance of polysulfide sealant vulcanized by manganese dioxide and epoxy resin vulcanization systems. After being stored at 130°C for 7 days, the elongation at break of the polysulfide sealant vulcanized by manganese dioxide and epoxy resin decreased by approximately 35% and 80% respectively, and the corresponding hardness increased by 10% and 35%, respectively. The elongation at break and tensile strength results of the polysulfide sealant vulcanized by manganese dioxide after air aging at 130°C is exhibited in Figure 2. The elongation at break of the polysulfide sealant decreased significantly after aging. Qin et al. [22] took the mechanical properties of a polysulfide sealant after being treated with No. 3 jet fuel at 150°C for 24 hours as a measurement index, and a single factor test method was used to investigate the effect of the antioxidant type, vulcanizing agent, filler and promoter on the aging resistance of the polysulfide sealant. Specifically, the vulcanizing agent is active manganese dioxide, the reinforcing filler is carbon black, and the antioxidant is 4020. The aging resistance of the polysulfide sealant is the best. Wang et al. [23] studied the influence of the type and amount of epoxy resin, liquid polysulfide rubber, filler, and antioxidant on the elongation of polysulfide sealant after aging with epoxy-modified liquid polysulfide sealant as the base adhesive. Through epoxy-modified polysulfide rubber, the tensile elongation and heat aging resistance of the polysulfide sealant can be effectively improved.

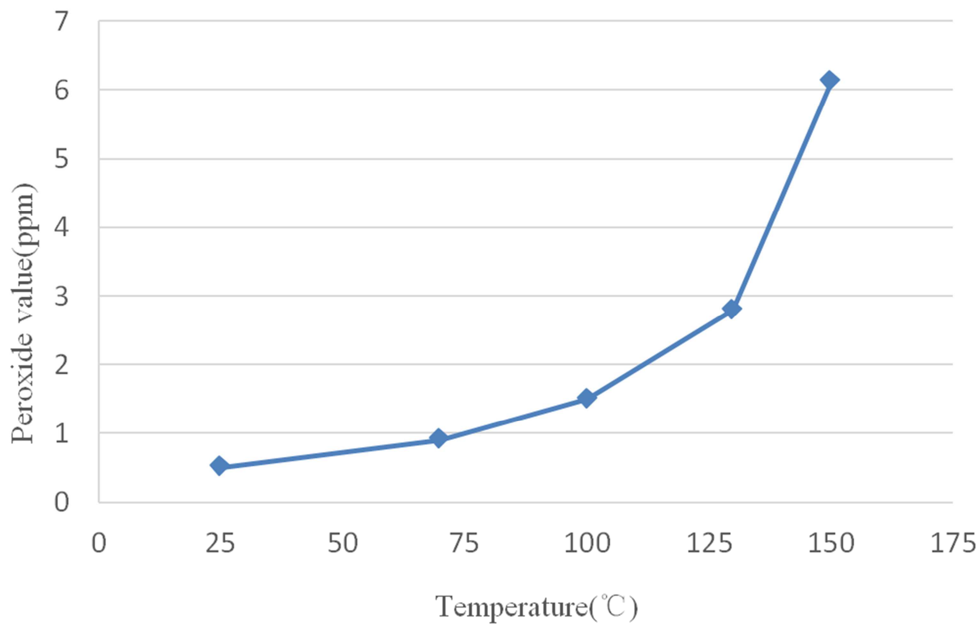

Figure 1. *Relationship between peroxide value and temperature of aviation kerosene.*

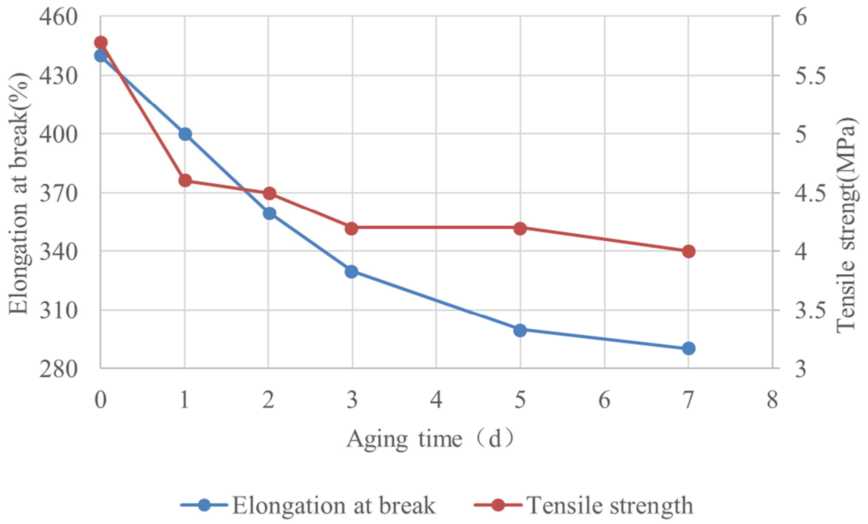

Figure 2. *Tensile Mechanical Properties after 130°C Heat-resistant Air Aging.*

3.2. Study on the Service Life Calculation Method of Sealants for Integral Fuel Tanks

At present, domestic research on aging and life determination of aviation rubber, sealant and other polymer materials has reached a certain level. A set of methods have been summarized in terms of material storage and service life estimation, and many experimental data and experiences have been obtained. Zhu et al. [24] used the rubber thermal oxidative aging method to evaluate the working capacity of aviation rubber and sealant after aging according to the aging empirical formula of rubber materials based on the Arrhenius equation and aging experimental data, and computer programming language was used to predict the life of aviation rubber and sealant. The service life of the XM-22B sealant and test 5880 sealant were predicted to be consistent with the measured values. Peng et al. [25] discussed the aging reaction process of polysulfide sealant via high-temperature aging experiments. The kinetic empirical formula and Arrhenius formula were used to linearly fit the experimental results. The aging activation energy of the polysulfide sealant and aging life at room temperature were extrapolated and calculated. The calculated aging activation energy of the polysulfide sealant was 78.783 kJ/mol, and the corresponding aging life was 35.8 years.

4. Study on the Corrosion of Sealants in Fuel Tanks

4.1. Study of the Corrosion Mechanism

In most cases, microorganisms prefer C_{10}-C_{18} carbon chain hydrocarbons as the nutrient source, and thus, aviation kerosene is more commonly contaminated by microorganisms than gasoline [26, 27]. Microbes can reproduce in jet fuel and metabolize to produce carbon dioxide, alcohol, grease, organic acids and other substances. Some microorganisms can also convert sulfide into sulfur, hydrogen sulfide and other active sulfur substances (such as sulfate-reducing bacteria and SRB), reducing the pH value and increasing the corrosion performance. Mold secretions can damage the surface protective coating and sealant of the aluminum alloy structure of the fuel tank. After 1000 flight hours, a large amount of white flocs appeared on the lower wall panel of the fuel tank, and the surface of the sealing adhesive layer had been corroded to varying degrees, as is shown in Figure 3.

Figure 3. *Sealing glue layer in the fuel tank of an aircraft after 1000 flight hours.*

Domestic scholars have the following views on the production of living sulfide by microbial metabolism [28, 29]: First, microorganisms propagate at the oil-water interface and in the tank bottom sediments, transforming inactive sulfides in jet fuel into active sulfides, causing corrosion of jet fuel. Second, the sulfide contained in the fuel additive will not reduce the pH of the fuel, and thiobacillus thiooxidans plays a major role. Thiobacillus thiooxidans grows and reproduces to produce sulfuric acid, which reacts with sulfide in the water layer to generate hydrogen sulfide and thus causes jet fuel corrosion [30]. The third is that SRB or sulfur-oxidizing bacteria generate hydrogen sulfide by using sulfide in tank bottom water, and hydrogen sulfide diffuses into the oil phase, resulting in corrosion of jet fuel. The action mechanism of microorganisms on jet fuel systems is not reliable and complete, especially the corrosion effect of microorganisms on polysulfide sealants, which needs further study.

4.2. Study on Anti-corrosion Measures

Microbial contamination in jet fuel will affect the combustibility, low-temperature fluidity, cleanliness and storage stability of fuel, increasing the corrosion of fuel, and may also pose a threat to aircraft flight safety. Strengthening oil quality management mainly involves strengthening the control of moisture, avoiding the invasion of dust and impurities in the air, and conducting regular microbial testing of the oil storage system [31]. The influence of microbial corrosion on the tank structure and sealing adhesive layer of the overall fuel tank can be determined by controlling the fuel quality, cleaning the fuel tank, and tank sterilization [32, 33]. Three kinds of mold inhibitors, including thiazole, organic metal complex, and imidazole were selected for application to the polysulfide sealant, and the antimold effect of the polysulfide sealant were investigated. The effect of the mold inhibitor on the technological and mechanical properties of the sealant was studied, indicating that the overall performance of the polysulfide sealant with added thiazole fungicides was optimal. Make necessary improvements based on the Civil Aviation Aircraft Maintenance Manual (AMM) and specify the specific requirements for pollution level classification, cleaning and sterilization of fuel tanks and accessories [34]. The corresponding sterilization process of civil aviation aircraft is shown in Figure 4.

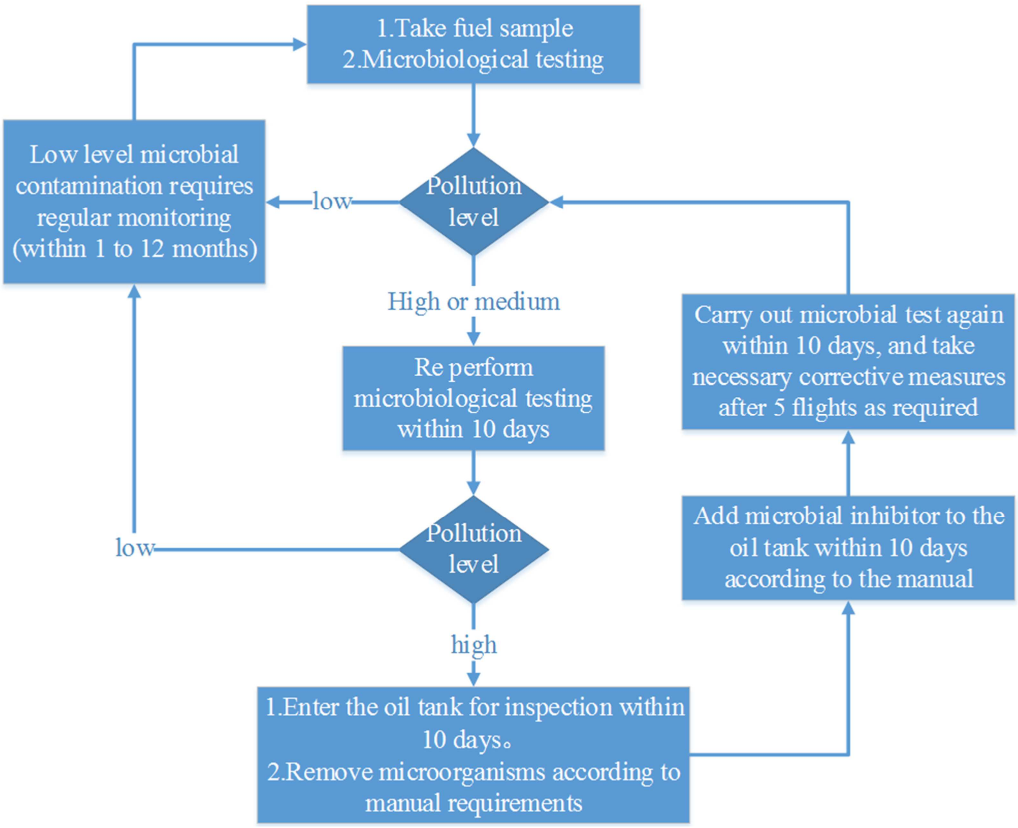

Figure 4. *Sterilization process of civil aviation aircraft.*

5. Conclusion and Prospects

(1) The sealant used for sealing of the integral structure oil tank is mainly polysulfide sealant, and domestic polysulfide sealant started late, lacking basic research on sealing.

(2) The aging of polysulfide sealant in aviation kerosene belongs to thermal oxidation aging. After aging, the strength and elasticity of the sealing adhesive layer

decrease significantly. Although the aging problem of polysulfide sealant cannot be prevented, the polysulfide sealant can be modified by adding filler or antioxidant, which can effectively improve the elongation at break and heat aging resistance of polysulfide sealant.

(3) Microbial corrosion has become the most serious and common problem of the overall fuel tank, which can be effectively prevented by controlling the fuel quality, cleaning the fuel tank, and sterilizing the fuel tank. The action mechanism of microorganisms on jet fuel systems is not reliable and complete, and the corrosion effect of microorganisms on polysulfide sealants needs further study.

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