

Analysis of the Environmental Parameters for Aircraft Coatings

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Summary: Temperature, UV radiation and pollutants play a major role in the degradation of aircraft coatings. The UV radiation at flying altitude is more intense than at ground level. An analysis of the radiation spectrum was used to choose the appropriate lamp type for artificial weathering in the laboratory. For the pollutants we examined the fact that the service life of aircraft coatings was considerably reduced in the years following the eruption of the volcano Pinatubo. It is shown that sulphuric-acid-aerosol droplets dispersed in the stratosphere were the main cause for that damage.

Keywords: aircraft coatings, degradation, environmental parameters, sulphuric acid aerosol, service life prediction

Introduction

Aircraft coatings have both protective and aesthetic functions. The paint has to shield the aircraft against corrosion and environmental effects thus making them safer and more durable. The aesthetical appearance is also very important because the aircrafts carry the company logos and colours to the airports throughout the world.

Aircraft coatings are subjected to rather severe environmental conditions. The temperature, UV radiation and pollutants are known to play a major role in degradation of the airspace coatings. The air temperature differences exceed 100 °C, ranging from - 60 °C (-76 °F) at a flying altitude of 10 km ^[1] to over 50 °C (104 °F) in airports located in tropical desert regions.^[2] Moreover, it is known that the coating surface temperature is much higher than the air temperature, especially for dark colours. ^[3] Apart from the temperature and UV, wetness is also a known factor influencing the life of coatings. This paper, the first one to our knowledge, gives an understanding to the phenomena of the damages of the aircraft coatings in the years from 1992 to 1995. During this

period of time the majority of aircraft coatings had only half of the expected service life: instead of usual 4 to 5 years in service the coatings became aesthetically unacceptable and lost some of their protective function much faster. It was found that the cause of these damages was the eruption of volcano Pinatubo in 1991,^[4] which had injected more than 20'000'000 tons of SO₂ into the stratosphere,^[5] the atmospheric layer above the clouds, in which lowest level the commercial air traffic takes place.

The purpose of the paper is the evaluation of the environmental parameters and their ranges for estimation of the service life for aircraft coating which will be the subject of the following papers. In this paper we will focus our attention mostly on the UV radiation and pollutants.

Influence of UV radiation on aircraft coatings

Sunlight is a very important factor for the ageing of aircraft coatings. It is known that the ultraviolet part is the main cause of the photo-oxidative degradation of coatings. The UV exposure data are available from several sources. One of them which gives a worldwide overview is available from satellite recording.^[6] Another source, UV-intensity broadband data measured on the ground are available from the database "Baseline Surface Radiation Network" at the sites placed all over the world,^[7] as shown in Figure 1. The following UV data are available from this database: UV-A global, UV-B direct, UV-B global, UV-B diffuse and UV-B upward reflected. For analysis of the ageing of aircraft coatings the UV-A data are of most interest.

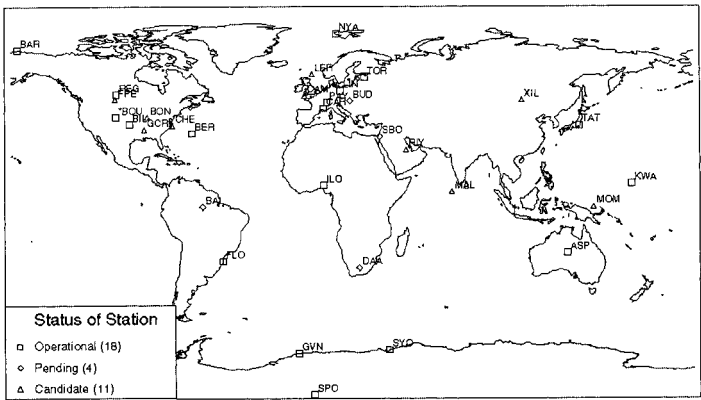


Figure 1. Stations of the Baseline Surface Radiation Network (denoted as letters)

The UV data for different wavelengths can be downloaded from Ref. 8 for some sites in the USA, Canada and New Zealand (Figure 2). These data are especially informative and useful for investigation of ageing processes in coatings when the wavelength sensitivity of a material is known.

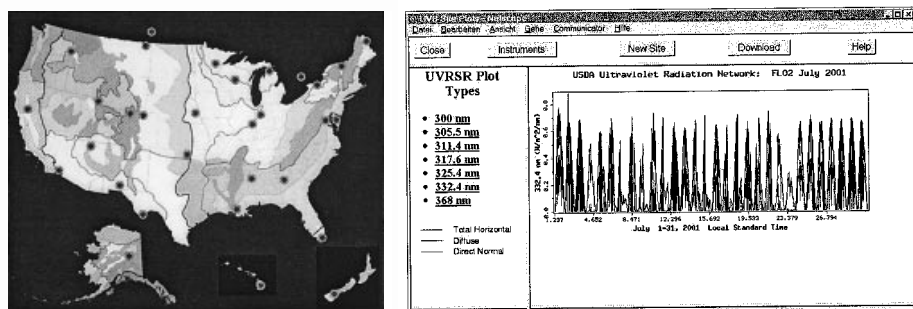


Figure 2. Test sites for which the UV intensity data are available (left). UV-intensity data for some wavelengths for one of the sites (Homestead in Florida) (right)

Aircraft coatings at a flying altitude of 10 km are subjected to more intensive radiation than the coating used on the ground: for example for a wavelength of 340 nm it is approximately 4 times more (see Figure 3).

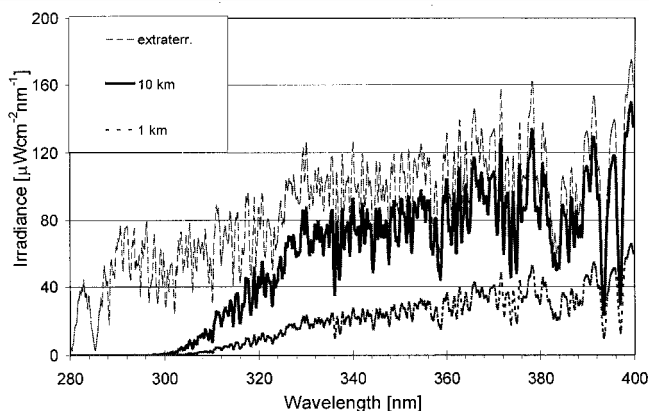


Figure 3. Spectral irradiance of sunlight for different altitudes calculated with the program MODTRAN 3.7 by the World Radiation Centre (WRC) in Davos in Switzerland^[9] assuming the zenith angle of 45°, based on the measured data obtained for the site Payerne (altitude 500 m) in Switzerland in May 1998

For reliable accelerated tests for aircraft coatings one should use a suitable light source that could reproduce the sun radiation at the 10-km altitude (Figure 3, black line). Basic accelerated testing procedures have been reviewed by Wypych.^[10] One of them uses high intensity sunlight focused on the sample using Fresnel mirrors with periodic exposure to moisture. The second type of accelerated test chambers employs UV fluorescent bulbs together with a dark condensing humidity cycle. The most common bulbs are the 340-UVA and 313-UVB. The third weathering chamber for coating evaluation is the one based on a xenon light source. All these procedures were discussed by Bauer^[3] concerning the accelerated ageing of automotive coatings. He concluded that tests based on fluorescent bulbs at 313-UVB or on Xenon with the quartz-boro or boro-boro filters are inappropriate for predicting in-service performance. All of them contain UV light that is shorter than that observed outdoors: up to 275 nm, 280 nm and 290 nm for UVB, Xenon quartz-boro and Xenon boro-boro, respectively. Fluorescent 340 UVA bulbs are a better match to sunlight between 300 and 360 nm, however the lack of long wavelength UV and visible light has implications for some specific failure modes.^[3]

For accelerated tests for aircraft coatings the choice of 340-UVA lamps seems to be the best as one can see from Figure 4: in the range 300-370 nm the intensity distribution of the 340-UVA bulb matches perfectly that at the 10 km altitude.

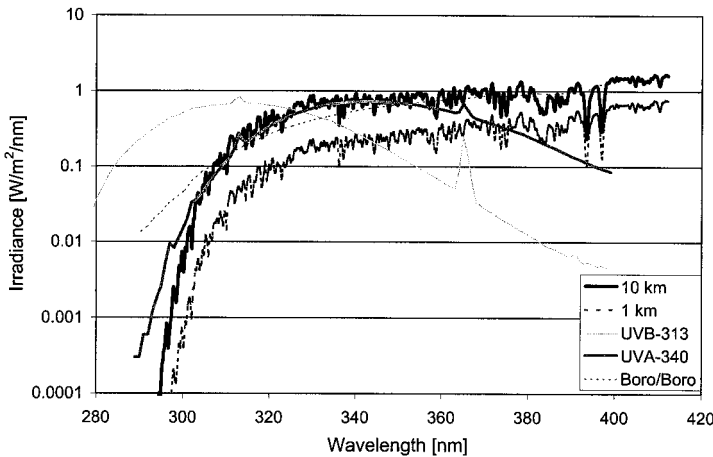


Figure 4. Spectral irradiance of sunlight at altitudes of 1 km and 10 km taken from Figure 3 compared to spectral irradiance of the 340-UVA and 313-UVB bulbs

Influence of sulphuric aerosol on aircraft coatings

For pollutants, we examine the fact that the service life of aircraft coatings was reduced by approximately 50% in the years from 1992 to 1995 following the eruption of the volcano Pinatubo in Philippines in June 1991. The eruption column reached 35 km in height and placed a giant cloud in the middle of the lower stratosphere extending to 1'100 km in diameter. During the eruption 15 to 20 megatons of SO_2 were injected into the stratosphere (Figure 5) and with the time dispersed all over the world reaching the maximal level of approximately 15 ppbv at around 26 km altitude on 21 September 1991.^[11] Within the next four months the concentration of SO_2 in the stratosphere measured in the Microwave Limb Sounder (MLS) experiment on the Upper Atmosphere Research Satellite (UARS) had gradually decreased toward its usual value 0.01 - 0.05 ppbv^[12] as shown in Figure 6.^[12]

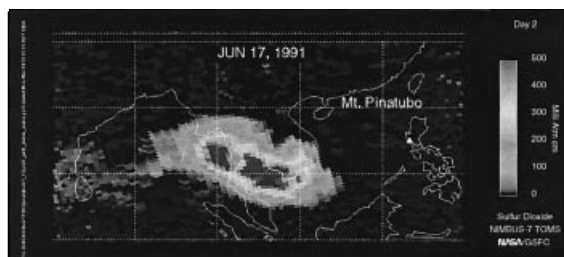


Figure 5. Distribution of SO_2 two days after eruption obtained using TOMS (Total Ozone Mapping Spectrometer)

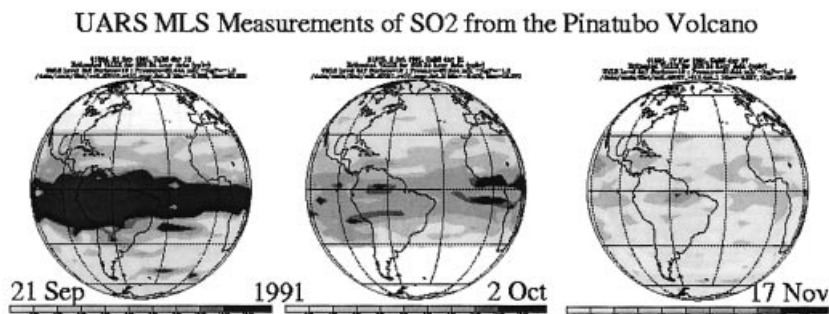


Figure 6. Change in distribution of SO_2 at 26 km from 21 September to 17 November 1991

It is known that SO_2 injected into the stratosphere is oxidised to sulphuric acid, which then forms aerosols through heteromolecular homogeneous nucleation of H_2SO_4 and H_2O vapours.^[12] The detailed review on the widespread impact of the Mount Pinatubo eruption by considering the stratospheric injection and mass of the aerosol-generating sulphur gases (primarily SO_2), the transport of the eruption cloud and conversion of SO_2 to stratospheric sulphate aerosols, and the effects of this aerosol level on radiation, weather, and climate was done in Ref. 5. It was pointed out there that about 20 to 30 megaton of sulphate aerosol droplets produced by Pinatubo eruption caused the largest perturbation to the stratospheric aerosol layer since the eruption of Krakatau in 1883. The aerosol cloud spread rapidly around the Earth in about 3 weeks and attained global coverage by about 1 year after the eruption. Peak local midvisible optical depths^[13] of up to 0.4 were measured in late 1992, and globally averaged values were about 0.1 to 0.15 for 2 years. One set of satellite data that has the capability of providing information about stratospheric aerosols is obtained by the solar occultation satellite instruments, the Stratospheric Aerosol and Gas Experiment (SAGE) I and the SAGE II (see Figure 7).

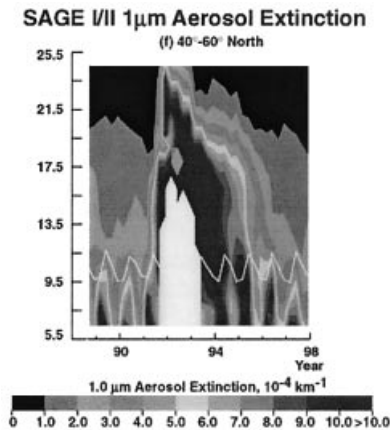


Figure 7. Aerosol concentration in the stratosphere derived from SAGE I and SAGE II.^[14] The data products consist of seasonally averaged values for the 1020 nm aerosol extinction^[15]

As follows from Figure 7, the aerosol content in the stratosphere at a flying altitude of about 10 km was still high in the years following the eruption up to 1997.

The question arises about the frequency of volcano eruptions that have influence on aircraft coatings. It is known that there are seldom periods without volcanic activity on the Earth.^[16]

However, there is a big difference in the power of volcano eruptions. The biggest volcanoes that have had influence on the stratosphere since 1850 are shown in Figure 8.

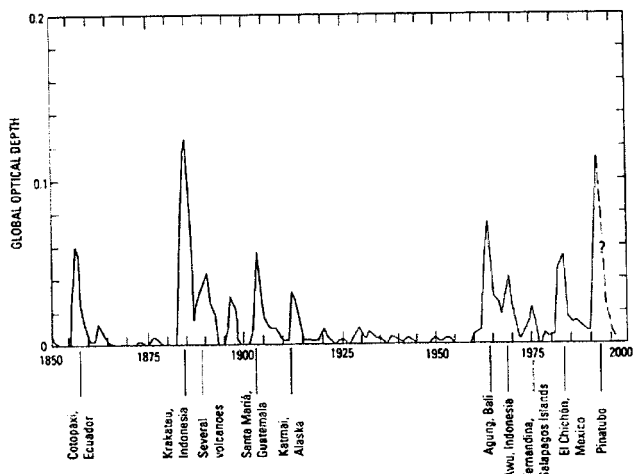


Figure 8. Estimated global optical depth at $\lambda = 0.55 \mu\text{m}$ for the period 1850 to 1993, after Sato et al.^[17] Most peaks are the result of instantaneous volcanic injections of SO_2 into the stratosphere and subsequent rapid formation and monotonic decline of sulphate aerosols.

It follows from Figure 8 that the last big volcano eruption comparable to Pinatubo was Krakatau eruption in August 1883, which also produced an aerosol veil of global extent. In fact, the maximum 20 to 30-Mt Pinatubo stratospheric aerosol loading may be not that much smaller than Krakatau's, variously estimated at between 30 and 50 Mt.^[5]

Although large volcano eruptions which inject considerable amount of aerosol into the stratosphere are rather seldom events, they have dramatically influence on the aircraft coating during the following years. This aspect should be taken into account in the development of new formulations for aircraft coatings.

Quantitative description of environmental parameters for service life prediction for aircraft coatings

All the environmental parameters discussed above vary steadily depending on the day-night cycle, season, year etc. In order to use them for Service Life Prediction (SLP) for organic coatings, an averaging has to be done.

For the SLP for automotive paints Bauer used the following approach.^[3,18-19] For the photo-oxidative degradation, he introduced the time unit *Photo – ox _Extent* [Exposure Time Equal to One Years in Florida], which is

$$Photo - ox_Extent = C \int_0^1 I(t) e^{\frac{-E_a}{RT(t)}} dt, \tag{ 1 }$$

Here the UV-light intensity $I(t)$ is multiplied with the Arrhenius term $e^{\frac{-E_a}{RT(t)}}$ with the temperature T and integrated over time t . E_a is between 5 and 8 kcal/mol, the gas constant $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and C is a constant with the unit ["Exposure Time Equal to One Years in Florida" / "Intensity" * "time"]. The influence of wetness was treated in Bauer's work,^[18] with a weighting factor for each exposure site.

A similar approach was used by Jorgensen et al.^[20] for the service life prediction for clear coat/coloured basecoat paint systems. The following generalised cumulative dosage model for the loss in performance, ΔP , was used:

$$\Delta P(t) = A \int_0^t [I_{UV}(\tau)]^n e^{-E/kT(\tau)} d\tau \tag{ 2 }$$

where I_{UV} is the cumulative UV light dosage integrated over a bandwidth of 290-385 nm; A , n , E are fitting parameters, where E denotes the activation energy; k is the Boltzmann constant. Depending on the system, the values 3.8 - 8.4 kcal/mole-K for activation energy and 0.67 - 0.71 for n were obtained.

Based on the work above, the Arrhenius relationship should be used for the averaging of the temperature and a power law seems to be a good approximation for the UV radiation. Therefore, for the first estimation we are going to use the following averaging, where the whole time interval is represented by a sum of m subintervals for the temperature and the UV intensity, respectively,

$$\bar{T} = \frac{\sum_i^m (T(t_i) \cdot p(t_i))}{\sum_i^m p(t_i)} \qquad \bar{I} = \frac{\sum_i^m (I(t_i) \cdot p(t_i))}{\sum_i^m p(t_i)}, \tag{3}$$

where the weighting function has the form

$$p(t) = I_{UV(at340nm)}^n \cdot e^{-[E_a/RT(t)]} \cdot \Delta t. \tag{4}$$

Calculations were made using the above approach with the averaging over one year. As input, monthly averaged temperature for some destination sites in the USA, Europe, Far East and Africa were taken. An assumption of flying time of 62 % was made. The value for the activation energy E_a in Eq. (4) was 153 kcal/mol, which was within the interval 129 - 180 kcal/mol (30.8 -43.1 kJ/mol) obtained by Allen et al.^[21] but differed from the values of 5 - 8 kcal/mol used by Bauer^[3] and Jorgensen et al.^[20] The parameter n in Eq. (4) was 0.6, which was close to that used by Jorgensen et al.^[20] but differed from 1, assumed by Bauer^[3]. Both values were obtained as fitting coefficients for a stress-life relationship in accelerated weathering test for a reference polyurethane coating. In the following papers we will describe the procedure in details.

Using the above approach the estimated averaged value for the temperature is 19.3 °C, whereas that for the UV-parameter is 0.23 W/(m² nm). Both values will be used as service conditions or so-called "use level" values in the further calculations of the service life for organic coatings.

Conclusions

In this work the analysis of the environmental parameters relevant to aircraft coatings was done. The following parameters were considered: temperature, UV radiation and sulphuric aerosol. The first parameter, the air temperature, ranges from - 60 °C at flying altitude to over 50 °C in airports located in tropical desert regions.

The second parameter, UV radiation at flying altitude, is more intense than at ground level: for example, for a wavelength of 340 nm it is approximately 4 times more. From the analysis of the radiation spectrum at flying level follows that in the range 300-370 nm the intensity distribution of the 340-UVA bulb matches perfectly to that at the 10-km altitude. Therefore for the artificial weathering of the aircraft coatings in the laboratory these bulbs have to be used.

For the third parameter, pollutants, we examined the fact that the service life of aircraft coatings was reduced by approximately 50% in the years following the eruption of the volcano Pinatubo when more than 20 Megatons of SO₂ were dispersed into the stratosphere. In this work it is shown that the resulting 25-30*10⁹ kg H₂SO₄-aerosol droplets were a main cause for damage to aircraft coatings during the four years following the eruption.

Humidity as a stress parameter was excluded from considerations because the variation of this

parameter across different aircrafts flying long-range routes is not so distinguishable.

All the analysis above was done to find out the quantitative description of the environmental parameters for use in the service life prediction for organic coatings and for construction of the weathering device that can simulate the ageing of the aircraft coatings in a proper way. The estimated averaged value for service-conditions or so-called "use level" value for the temperature is 19.3 °C, whereas that for the UV-parameter is 0.23 W/(m² nm). Both values will be in the further calculations of the service life for organic coatings.

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