Low Earth Orbital Atomic Oxygen Interactions With Materials

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Summary

Atomic oxygen is formed in the low Earth orbital environment (LEO) by photo dissociation of diatomic oxygen by short wavelength (< 243 nm) solar radiation which has sufficient energy to break the 5.12 eV O₂ diatomic bond in an environment where the mean free path is sufficiently long (~ 10⁸ meters) that the probability of reassociation or the formation of ozone (O₃) is small. As a consequence, between the altitudes of 180 and 650 km, atomic oxygen is the most abundant species. Spacecraft impact the atomic oxygen resident in LEO with sufficient energy to break hydrocarbon polymer bonds, causing oxidation and thinning of the polymers due to loss of volatile oxidation products. Mitigation techniques, such as the development of materials with improved durability to atomic oxygen attack, as well as atomic oxygen protective coatings, have been employed with varying degrees of success to improve durability of polymers in the LEO environment. Atomic oxygen can also oxidize silicones and silicone contamination to produce non-volatile silica deposits. Such contaminants are present on most LEO missions and can be a threat to performance of optical surfaces. The LEO atomic oxygen environment, its interactions with materials, results of space testing, computational modeling, mitigation techniques, and ground laboratory simulation procedures and issues are presented.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Aₖ</td>
<td>surface area of Kapton® witness sample exposed to atomic oxygen (cm²)</td>
</tr>
<tr>
<td>Aₛ</td>
<td>surface area of the flight sample exposed to atomic oxygen attack (cm²)</td>
</tr>
<tr>
<td>Eₖ</td>
<td>erosion yield of Kapton® witness sample (3.0 x 10⁻²⁴ cm³/atom)</td>
</tr>
<tr>
<td>Eₛ</td>
<td>erosion yield of flight sample (cm³/atom)</td>
</tr>
<tr>
<td>F</td>
<td>fluence of atomic oxygen (atoms/cm²)</td>
</tr>
<tr>
<td>ΔMₖ</td>
<td>mass loss of Kapton® witness sample (g)</td>
</tr>
<tr>
<td>ΔMₛ</td>
<td>mass loss of the flight sample (g)</td>
</tr>
<tr>
<td>ρₖ</td>
<td>density of Kapton® witness sample (1.42 g/cm³)</td>
</tr>
<tr>
<td>ρₛ</td>
<td>density of sample (g/cm³)</td>
</tr>
</tbody>
</table>

I. Atomic Oxygen Effects

A. Environment Description

Atomic oxygen (AO) is formed in the low Earth orbital environment (LEO) by photo dissociation of diatomic oxygen. Short wavelength (< 243 nm) solar radiation has sufficient energy to break the 5.12 eV O₂ diatomic bond (ref. 1) in an environment where the mean free path is sufficiently long (~ 10⁸ meters) that the probability of reassociation or the formation of ozone (O₃) is small. As a consequence, between the altitudes of 180 and 650 km, atomic oxygen is the most abundant species (fig. 1) (ref. 2).
Although excited states of atomic oxygen can be formed, their lifetimes are sufficiently short that the 3P ground state dominates the LEO atomic oxygen formation and is dependent upon the diatomic oxygen density and solar UV flux. Solar heating of the Earth’s atmosphere causes an increase in the number density of atoms at a given altitude as the Earth rotates from sunrise toward solar noon. Because the atmosphere co-rotates with the Earth, the solar heated bulge in the atmosphere is pushed forward such that the peak of the atomic oxygen density occurs at approximately 3 P.M. rather than solar noon. As a consequence, anti-solar facing surfaces such as the back side of solar arrays receive 25 percent more atomic oxygen fluence than the solar facing surfaces as the spacecraft orbits the Earth (ref. 3).

Solar-caused variations in the ultraviolet radiation impinging upon the LEO atmosphere can greatly change the atomic oxygen production rate (and therefore the arriving flux on spacecraft surfaces). Periods of high and low solar activity can change the arriving flux by a factor of up to 500 depending on altitude (fig. 2) (ref. 2). Thus the atomic oxygen flux cannot be accurately predicted due to uncertainty in the solar activity. The average atomic oxygen fluence per year varies as a result of the solar activity consistent with the 11 years sun spot cycle as shown in figure 3, based on the MSIS–86 atmospheric model (ref. 4). Atomic oxygen can also be produced in other planetary environments where oxygen is present.
Figure 2: Atomic oxygen flux versus altitude for solar minimum, nominal (standard atmosphere), and solar maximum conditions.

Figure 3: Atomic oxygen fluence per year during a solar cycle.
As a spacecraft orbits the Earth at velocities on the order of 7.7 km/sec, it runs into the atomic oxygen (hence the term, “ram” atomic oxygen). If the spacecraft is in an orbit that has zero inclination then the average angle of attack of the atomic oxygen is perpendicular to surfaces whose surface normal points in the direction of travel. However, most spacecraft have orbits which are inclined with respect to the Earth’s equatorial plane. This causes the average angle of attack of the arriving atomic oxygen to sinusoidally vary around the orbit as a result of the vectoral addition of the orbital spacecraft velocity vector and the atmosphere’s co-rotation velocity vector (ref. 5). In addition, atomic oxygen atoms have thermal velocities associated with their Maxwell Boltzman velocity distribution at the high temperatures of LEO which are typically ~1000 K (ref 2). The high velocity tail of the Maxwell Boltzman distribution actually allows some atomic oxygen atoms to catch up with the trailing surfaces of a LEO spacecraft to produce a small flux which is orders of magnitude lower than the ram flux. If one adds the three vectoral components and averages over a typical 400 km orbit at 28.5° inclination, then angular distribution of arriving atoms is as shown in figure 4, where the arrival distribution in the horizontal plane is shown as a function of incidence angle for surfaces normal to the ram direction (ref. 6). Atomic oxygen can arrive at angles beyond 90° from the orbital direction. For example, figure 5 shows that a surface whose normal is 90° with respect to the ram direction receives approximately 4 percent of the flux that occurs for a surface whose normal is parallel to the ram direction. The impact energy of arriving atomic oxygen atoms also is dependent upon the following three contributions to the resulting velocity vectors: the orbital spacecraft velocity, the Earth’s atmosphere co-rotation velocity, and atomic oxygen thermal velocity.

Figure 4: Atomic oxygen arrival flux relative to the ram direction for a 400 km orbit at 28.5° inclination and 1000 K thermosphere
Figure 5: Polar plot of relative atomic oxygen flux as a function of the angle between the ram direction and the normal of the arrival surface for a LEO spacecraft in a 400 km orbit at 28.5° inclination and 1000 K thermosphere
Figure 6: Energy distribution of atomic oxygen atoms as a function of altitude for a circular orbit at 28.5° inclination and 1000 K thermosphere

Figure 6 is a plot of the energy distribution of atomic oxygen atoms as a function of altitude for a circular orbit with 28.5° inclination and 1000 K thermosphere (ref. 7). As can be seen, the average impact energy is 4.5 eV ± 1 eV for a 400 km orbit and the impact energy decreases with altitude. For highly elliptical orbits, the perigee ram impact energy can be significantly higher than for circular LEO orbits. Such elliptical orbits can also produce high fluxes near perigee due to the low altitudes involved. If a spacecraft is spinning with its axis of rotation perpendicular to the Earth then the average flux to any surface is simply $1/\pi$ of that of the ram direction.

B. Interaction with Materials

Although LEO atomic oxygen possesses sufficient energy to break most organic polymer bonds and sufficient flux to cause oxidative erosion of polymers, there was little known or interest in atomic oxygen interaction with materials until the start of space shuttle missions. This is primarily because most prior missions occupied high altitude orbits where atomic oxygen densities are rather inconsequential.

One evidence of LEO environmental interaction with materials is the glow phenomena that occurs when atomic oxygen and other LEO atmospheric species impact spacecraft surfaces causing the creation of short-lived excited state species that emit visible radiation near the surfaces of spacecraft as shown in figure 7, where 7(a) was taken during the daylight and 7(b) was taken as a time exposure at night (refs. 8 to 10).
(a) Photograph of space shuttle during daylight

(b) Photograph of space shuttle at night

Figure 7: Low Earth orbital glow phenomena
The reaction of atomic oxygen with spacecraft materials has been a significant problem to LEO spacecraft designers. Atomic oxygen can react with polymers, carbon and many metals to form oxygen bonds with atoms on the surface being exposed. For most polymers hydrogen abstraction, oxygen addition or oxygen insertion can occur (fig. 8).

With continued atomic oxygen exposure, all oxygen interaction pathways eventually lead to volatile oxidation products accompanied by the gradual erosion of hydrocarbon materials. Surfaces of polymers exposed to atomic oxygen also develop an increase in oxygen content as shown in figure 9 (ref. 11).
Figure 9: Surface oxygen content (measured using XPS) for chlorotrifluoroethylene as a function of atomic oxygen exposure level, where exposures were conducted in ground facility RF air plasma.

The sensitivity of hydrocarbon materials to reaction with atomic oxygen is quantified by the atomic oxygen erosion yield of the material. The atomic oxygen erosion yield is the volume of a material that is removed (through oxidation) per incident oxygen atom. The most well-characterized atomic oxygen erosion yield is that of polyimide Kapton H which has an erosion yield of $3.0 \times 10^{-24} \text{ cm}^3/\text{atom}$ for LEO 4.5 eV atomic oxygen (refs. 12 and 13). Table 1 (from refs. 14 to 16) lists the atomic oxygen erosion yields of a wide variety of polymers, where many of the values are measured from space experiments and others are predicted values. The predicted erosion yield values ($\gamma'$ mod-Correlation and 1/OI Correlation (ref. 16)) listed in table 1 were made based on predictive models, developed for the interaction of polymers with the LEO environment, and using information about the chemical composition, structure, and densities, as well as experimental data for Oxygen Index (OI) (ref. 17).

The most common technique for determining the erosion yield of flight samples is through mass loss measurements. These measurements are made by obtaining mass measurements of the sample before and after flight. The erosion yield of the sample, $E_S$, is calculated through the following equation:

$$E_S = \frac{\Delta M_s}{(A_s \rho_s F)}$$

where

$E_S = \text{erosion yield of flight sample (cm}^3/\text{atom})$

$\Delta M_s = \text{mass loss of the flight sample (g)}$

$A_s = \text{surface area of the flight sample exposed to atomic oxygen attack (cm}^2)$
\( \rho_s \) = density of sample (g/cm\(^3\))

\( F \) = fluence of atomic oxygen (atoms/cm\(^2\))

The atomic oxygen fluence, \( F \), can be determined through the mass loss of a Kapton\(^{\circledast} \) witness sample because Kapton\(^{\circledast} \) has a well characterized erosion yield in the LEO environment. Therefore, the atomic oxygen fluence can be calculated using the following equation:

\[
F = \frac{\Delta M_K}{(A_K \rho_K E_K)}
\]

where

\( \Delta M_K \) = mass loss of Kapton\(^{\circledast} \) witness sample (g)

\( A_K \) = surface area of Kapton\(^{\circledast} \) witness sample exposed to atomic oxygen (cm\(^2\))

\( \rho_K \) = density of Kapton\(^{\circledast} \) witness sample (1.42 g/cm\(^3\))

\( E_K \) = erosion yield of Kapton\(^{\circledast} \) witness sample (3.0 \times 10^{-24} \text{ cm}^3/\text{atom})

Thus

\[
E_S = E_K \frac{\Delta M_S A_K \rho_K}{\Delta M_K A_S \rho_S}
\]

One of the critical issues with obtaining accurate erosion yield data from mass loss measurements is making sure that dehydrated mass measurements are taken. Many polymer materials, such as Kapton\(^{\circledast} \), are very hygroscopic (absorbing up to 2 percent of their weight in moisture) and can fluctuate in mass significantly with humidity and temperature. Therefore, for accurate mass loss measurements to be obtained, it is necessary that the samples be fully dehydrated (e.g. in a vacuum desiccator) prior to measuring the mass both pre-flight and post-flight.

There is a large variation in the erosion yield values for the space data provided in table 1. This is because some flight experiments were exposed to low atomic oxygen fluences on-orbit, such as during a shuttle flight experiment. Variations in much of the early LEO space data also as occurred because some erosion yield data were not determined based on dehydrated mass measurements, introducing large error for hygroscopic materials, especially for low fluence exposures or low erosion yield samples. The erosion yield values listed in table 1 from references 15 and 16 represent more recent erosion yield values.

A LEO environment experiment called the MISSE (Materials International Space Station Experiment) PEACE (Polymers Erosion and Contamination Experiment) Polymers contains 41 different polymers for long term atomic oxygen erosion determination (ref. 18). The MISSE PEACE Polymers samples were placed on the outside the ISS Quest Airlock in August 2001 during shuttle mission STS–105. The experiment is scheduled to be retrieved during STS–114, more than three years after its installation on ISS. The erosion yield data (to be obtained using dehydrated pre- and post-mass measurements) from this long-term International Space Station (ISS) experiment will be directly compared with the predictions provided in table 1.

Atomic oxygen can also oxidize the surfaces of metals to produce nonvolatile metal oxides. However, for most metals, the oxides tend to shield the underlying metal from oxidation. Silver is one exception, because silver oxide tends to spall from the underlying metal thus allowing continued oxidation. Such effects caused silver solar cell interconnects to fail in LEO (ref. 13). Atomic oxygen interaction with silicones causes oxidation and removal of methyl groups and gradual conversion of the surface of silicones to silica (refs. 19 to 21). This frequently results in shrinkage and crack formation in the exposed silicones (figs. 10 and 11) as they are transformed from low modulus polymers into the higher modulus silica.
Surfaces of materials with volatile oxidation products (such as hydrocarbon polymers), that are oriented in a fixed position with respect to the ram direction gradually develop left-standing cones which point in the direction of arriving atomic oxygen. Thus the microscopic roughness of the surfaces increases with time. Because the erosion of one location is independent of any other location and atomic oxygen arrives randomly, the development of surface roughness obeys Poisson statistics. This causes the surface roughness to increase as the square root of the atomic oxygen fluence (ref. 22). Figure 12 shows typical atomic oxygen textured surfaces of Kapton® H polyimide, fluorinated ethylene propylene and chlorotrifluoroethylene after fixed-orientation exposure to atomic oxygen in LEO (refs. 23 and 24).
In addition to polymer thickness loss, such texturing causes an increase in diffuse reflectance and a decrease in specular transmittance of polymers (ref. 25). Atomic oxygen exposure of hydrocarbon or halocarbon polymers that are pigmented or filled with metal oxide particles results in erosion of the polymeric content resulting in gradual exposure of an increasing surface population of metal oxide particles which are poorly attached to each other.
The metal oxide particles, which become loosely attached, gradually shield the underlying polymer content from atomic oxygen erosion. Thus the erosion yield can gradually decrease with atomic oxygen fluence.

C. Mitigation Techniques

Atomic oxygen erosion of thin polymers in LEO has represented a challenging spacecraft performance and durability problem for many years. Three approaches have been taken in efforts to reduce or eliminate atomic oxygen erosion of polymers. The three approaches to achieve polymer durability to atomic oxygen consist of: (1) the application of thin film protective coatings made of atomic oxygen durable materials, (2) the modification of the surface of the polymers to make them more durable to atomic oxygen, and (3) the use of alternative polymers that contain metal atoms which develop a protective coating with atomic oxygen exposure.

The first and most widely used mitigation approach is the application of thin film metal, metal oxide or fluoropolymer-filled metal oxide protective coatings to polymers (refs. 27 to 31). Thin film coatings of SiO$_2$, Al$_2$O$_3$, Indium Tin Oxide, Ge, Si, Al, and Au with thickness ranging from a few hundred to more than 100 nm are typically applied by sputter deposition or vapor deposition. For example, the SiO$_2$ coatings on Kapton® H polyimide for the solar array blankets on the International Space Station are 130 nm thick and applied by magnetron sputter deposition (ref. 32). Although metal oxide coatings as thin as ~5.0 nm can provide atomic oxygen protection on ultra smooth surfaces, usually thicknesses of ~100 nm are used to assure complete coverage over irregularities of debris, pits and rills on polymer surfaces. Coatings which are factors thicker than 100 nm can more easily crack or spall due to either their intrinsic stress or inability to conform with flexure compression or expansion at their polymer substrates. The addition of fluoropolymer content to metal-oxide coatings allows factors greater strain-to-failure in the coatings. Such coatings can be deposited by co-sputter deposition of SiO$_2$ and polytetrafluoroethylene Teflon® (refs. 25 and 27).

The atomic oxygen durability of polymers, that are protected by thin film coatings made of materials which are themselves atomic oxygen durable, is largely dependent upon the number and size of pinwindow and scratch defects in the protective coatings (fig. 13).

![Scanning electron microscope photographs of LEO atomic oxygen exposed Kapton® from the Long Duration Exposure Facility (LDEF) at sites of pinwindow and crack defects in a vacuum deposited aluminum protective coating after an atomic oxygen fluence of $8.99 \times 10^{21}$ atoms/cm$^2$ at 8.1 degrees off ram on row 9](image)

The application of 130 nm SiO2 protective coatings on Kapton® polyimide can frequently reduce the rate of weight loss due to atomic oxygen erosion of Kapton® to less than 1 percent of that of unprotected Kapton® (ref. 32). Atomic oxygen undercutting oxidation at sites of pin window and scratch defects can ultimately lead to mechanical failure of the polymer when a sufficient number of undercut cavities connect (ref. 29). The growth of undercut cavities has been studied for polymer films coated on one side or both sides through the use of Monte Carlo computational modeling (refs. 7, 33 to 36).
One approach to reducing the number of pinwindow and scratch defects in atomic oxygen protective coatings is to apply a surface tension leveling coating to the material prior to applying the protective coating. Studies have found the use of leveling coatings successful for increasing the atomic oxygen durability of protective coatings on composite materials based on decreasing defect densities (refs. 37 and 38). For example, in one study a low viscosity epoxy was applied to the surface of several composite coupons. A protective layer of 1000 Å of SiO₂ was deposited on top of the leveling coating, and the coupons were exposed to an atomic oxygen environment in a plasma asher. Pinhole populations per unit area were estimated by counting the number of undercut sites observed by scanning electron microscopy. Defect density values of 180,000 defects/cm² were reduced to about 1000 defects/cm² as a result of the applied leveling coating (ref. 37). Leveling coatings have also been found to improve the optical performance of composite concentrator surfaces by improving the specular reflectance (refs. 37 and 38).

The mitigation approach involving modification to the surface of polymers to make them more durable to atomic oxygen has primarily involved either implantation of metal atoms into the surface of the polymer (ref. 39) or chemical modification of the surface of the polymer to incorporate silicon atoms into the surface and near surface. In both surface modification approaches the degree to which the atomic oxygen erosion yield is reduced is dependent upon the aerial density of metal atoms that can be placed into the polymer surface.

The formation of alternative polymers that contain inorganic atoms has been approached through a variety of chemical formulations including the use of silicone co-polymers (ref. 40), polysilsesquioxane (ref. 41), cage coordination compound incorporation of metal atoms (ref. 42) and phosphorous containing polymers (ref. 43). As with the surface alteration approach, the durability of the alternative polymer is dependent upon the aerial density of inorganic atoms that can be achieved. In addition, the alternative polymers must achieve the durability to other space environmental threats such as UV radiation and ionizing radiation to be considered a suitable replacement for Kapton® polyimide. However, some of the alternative polymers have the advantage of much lower solar absorptance than Kapton® (ref. 43).

## II. Effects of Atomic Oxygen Interaction with Spacecraft Contamination

### A. Sources and Transport of Spacecraft Contamination

Spacecraft contamination can be defined as molecular or particulate matter on or near a spacecraft surface that is foreign to that surface. Sources of spacecraft contamination can include thruster propellants and burn residue, outgassing of spacecraft materials, vented gases from spacecraft systems, fluids released from the spacecraft by dumping or leakage, micrometeoroids and orbital debris, and particles generated or redistributed during spacecraft mechanical operations or astronaut extravehicular activity (EVA) operations (ref. 44). Comprehensive data on outgassing of spacecraft materials is found in reference 45. Space environment interactions with materials can also produce contaminants, such as volatile products of atomic oxygen reactions and ultraviolet-induced or radiation-induced chain scission products in polymer materials and residual non-oxidative films left free-standing due to AO erosion of underlying material. Space environment effects, such as atomic oxygen, ultraviolet, and radiation interactions, can further modify contaminant species.

Spacecraft contaminants can either deposit onto spacecraft surfaces or remain in the vicinity of the spacecraft. Molecular contaminants can transport from surface-to-surface through various mechanisms including line-of-sight transport, non-line-of-sight transport through reflection or scattering, and reattraction of positively ionized contaminants to a negatively charged, sunlit spacecraft surface (ref. 46). These transport mechanisms can put critical spacecraft surfaces at risk for contamination effects.

### B. Contamination Effects on Spacecraft Surfaces

Buildup of molecular or particulate spacecraft contamination can cause degradation in transmittance, reflectance, interactions with spacecraft contamination include AO oxidation of outgassed silicones to produce a non-eroding silica-based layer, and ultraviolet or ionizing radiation interactions with contaminants to produce a contaminant film. Examples of these cases will be solar absorptance, and thermal emittance of surfaces. The impacts of this degradation include reduced performance of solar arrays, radiators, instrument optics, sensors, and other systems (ref. 44).

Some particularly detrimental cases of space environment discussed below.

#### 1. Atomic Oxygen Interaction with Silicones

Almost all spacecraft have silicones on board in the form of adhesives, potting compounds and lubricants used in materials processing. Although most LEO spacecraft designers make efforts to use only silicones that are vacuum
stripped to eliminate or reduce the amount of volatile short chain content, silicone fragments are often evolved in the vacuum environment in LEO with the process being further enhanced with AO and/or radiation-induced bond breaking. The resulting silicone fragments can deposit on surfaces that are exposed to atomic oxygen. If the surfaces are not receiving atomic oxygen, then simple re-evaporation of the silicone can occur providing that the surfaces are the same temperature or hotter than the source of the silicone. Or, UV may interact with the silicone fragments causing a polymerized contaminant layer to build up. With atomic oxygen arrival, oxidation reactions cause the silicones to lose hydrocarbon content and convert to a silica-based surface layer which is resistant to atomic oxygen erosion. Such processes occurred on the MIR Space Station resulting in the accumulation (over a ten-year duration) of a microscopically rough coating on the solar array (fig. 14).

(a) Photograph showing silica contamination as a diffuse white deposit on the front surface of the solar cells

(b) Scanning electron microscope photograph of oxidized silicon contamination layer

Figure 14: MIR solar array sun facing surface after 10 years in LEO
Figure 15: Optical solar reflector on the back surface of a MIR solar cell after 10 years in LEO with tape peeled areas to show comparison of the “tape peeled cleaned” versus the contaminated optical solar reflector glass

Figure 15 is a photograph of the anti-solar side of the same MIR solar array which was up to 4.6 $\mu$m thick (ref. 19). Such coatings tend to be rather transparent. However if the silicone deposition is also accompanied by hydrocarbon deposition, a much more optically absorbing coating can result (ref. 47).

The contamination is much more absorbing. It appears as a tan colored silica deposit formed by atomic oxygen reaction of silicones that were arriving at the same time hydrocarbons could arrive from a polymer mesh behind the array. The contaminant layer was ~ 1.24 $\mu$m thick.

The Long Duration Exposure Facility (LDEF) satellite, which was exposed for 69 months in the LEO environment, provided an interesting study of contamination processes as the leading edge received a high fluence of directed ram AO along with solar exposure, and the trailing edge received very little AO along with similar solar exposure. The resulting molecular contamination process on LDEF was the removal of hydrocarbon based contaminants, and oxidation of silicone fragments on the leading edge (silica-rich, hydrocarbon-poor contaminant films), and the build-up of hydrocarbon contaminants and silicone fragments which were UV darkened on the trailing edge (hydrocarbon-rich, silicone contaminant films).
CONCLUDING REMARKS

The LEO atomic oxygen environment poses unique durability problems to spacecraft that are not witnessed in the normal atmospheric environment we live in. The energy and flux of highly reactive atomic oxygen can oxidize most polymers that are typically used in spacecraft manufacture. The results of the oxidation can lead to component structural failure, loss of thermal control or contamination depending upon the composition and function of the polymer. Thin film protective coatings can be effective in greatly reducing atomic oxygen erosion of polymers provided that their number scratch and pinwindow defects can be minimized. Atomic oxygen interactions with volatile silicones can result in the build up of silica deposits which can be optically absorbing if hydrocarbon volatiles are also present.

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