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SPACE MATERIALS TO PROTECT MINIATURE PHOTON COUNTING SYSTEMS USED IN LONG DURATION BALLONS FOR STRATOSPHERIC RESEARCH

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ABSTRACT

Optical resonance and fluorescence measurements, resulting from the photodissociation of atmospheric species, is an interesting method used in atmospheric and space research

Here we describe in detail the preliminary results of a lightweight photodetecting system that can be used to detect this light phenomena under severe temperature and pressure conditions. The obtained results are well adapted to make *in-situ* measurements with long duration stratospheric balloons. The very outgassing, contamination, weight and high dielectric characteristics of the silicone material found here can be widely used to protect stratospheric and planetary research instruments

RESUMEN

La medición de la resonancia óptica y de la fluorescencia que se produce por la fotodisociación molecular de algunos constituyentes atmosféricos es un método interesante a utilizar en la investigación atmosférica y espacial.

Aquí se describen detalladamente los resultados preliminares de un sistema "superligero" de conteo de fotones que puede ser utilizado para estudiar y detectar estos fenómenos luminosos, en condiciones extremas de temperatura y presión. Los resultados obtenidos están bien adaptados para efectuar mediciones *in-situ* con globos estratosféricos de gran duración. Las características de baja contaminación, baja pérdida de materia

por volatilización, el bajo peso, así como el alto coeficiente dieléctrico del silicón que se encontró, pueden ser ampliamente utilizados para proteger instrumentos de investigación estratosférica y planetaria.

1. INTRODUCTION

The study of the dynamical behavior of some stratospheric species such as O_3, H_2O_2, H_2O, NO_2 is frequently achieved with the aid of molecular photodissociation concepts [1,2] and with electronic systems that include photomultipliers and ultraviolet radiation sources. Their performance depends mostly on the capability of their separated devices and components to resist stratospheric temperature variations from +40 to -80°C. At the same time, one must take into account, that when a photomultiplier tube has very high operating voltages applied to its anode and dynodes, a gas ionization and arc phenomena might occur when the photodetecting system is operating under pressure values varying from 25 to 1 mb. These ionization problems have been avoided until now in stratospheric research [3], by the use of pressurised stainless steel containers that protect the instrument during all the flight period. However, this kind of solution is only used in stratospheric ballooning where the flight duration is limited to only one vertical excursion of less than 15 hours and where the load restrictions are almost without importance for a single *in-situ* experience. In the case of long duration ballooning requirements [4, 5, 6], another solution to this kind of inconveniences has to be found for photon counting devices which led us to adopt a space solution in the choice and research of a lightweight material that must prevent the arc phenomena, resist the huge temperature and pressure variations and have very low outgassing characteristics to prevent the contamination of the measurements. We think that silicone is the right material found after an extensive research, tests, and comparisions of different space materials, such as epoxies, urethanes, vinyls and others that have been used some times in the construction of space research instruments.

2. THE PHOTON COUNTING SYSTEM

Detailed description of the photodetector with its associated pulse shaping amplifier, charge sensible amplifier, electrical and functioning characteristics will be given somewhere else; here we only show a general block diagram on Fig. 1. It is composed of a H-292 Hamamatsu photomultiplier that detects energy over a spectral lenght going from 260 to 760 nm, with its quantum yield of 22% centered at a 330 nm wavelenght. It is followed by an Amptek-203 charge sensible amplifier and by an Amptek-206 pulse and wave shaping amplifier. The CSP has 4.4×10^{-4} coulumb sensitivity, being able to deliver a 200 mv amplitud signal with a 1.2 μ sec duration to the next amplifier stage which in turn generates a 10 volts amplitude square shaped signal with a 5 μ sec duration each time that a photoelectron hits the photomultiplier's sensible window. All the active and passive elements that we have grouped on this photon counting set are capable to operate from + 40 to -80°C, temperatures that are commonly found at ground and at 30 Km high. This spectral bandwidth can be used to

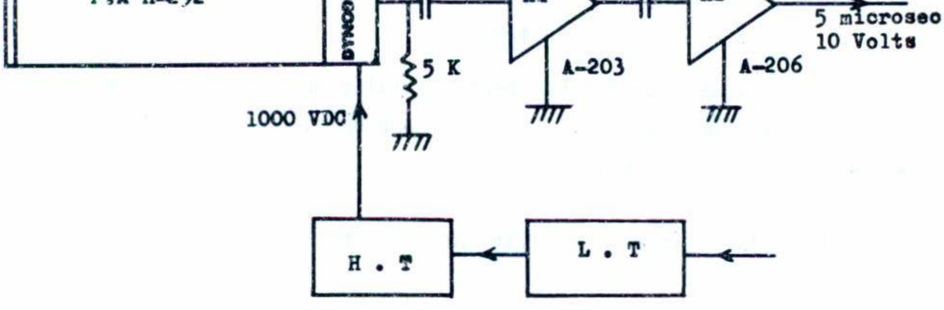

Fig. 1 Photon detector schematic diagram +42 and -80°C. Spectral range 200 to 700 nm.

detect luminiscence from the excited $OH(A^2\Sigma^+)$ radical when it is photodissociated from some polyatomic molecules according to the following reaction:

$$xyz + h\nu \longrightarrow xy^* + z \quad ,$$

in wich few milliseconds later xy* returns to its original state:

$$xy^* \longrightarrow xy + h\nu \quad .$$

The total density of the radicals can be determined with the following expression when the photodissociating energetic beam is considered chromatic:

$$[xy^*] = \frac{[xyz] \; \phi \; J}{T_p + \sum_i k_q^i \; [M_i]}$$

In this equation ϕ is the quantum yield that produces the excited fragments, T_p is the transition probability per second and k_q^i is the rate coefficient for quenching by the ith-component. If photolysis is made only with a monochromatic light source, the photodissociation coefficient is given by the product of the photon source flux ψ_λ and the absorption cross section σ of the xyz molecule at wavelenght λ:

$$J = \psi_\lambda \sigma \quad (s^{-1}).$$

Although this detector has been initially built with the purpose of measuring only the atmospheric H_2O, in long duration flights, after photodissociation according to (7):

$$H_2O + h\nu \; (\text{Lyman} - \alpha \;\; 1216 \; \mathring{A}) \longrightarrow OH \; (A^2 \; \Sigma^+) + H$$

and $\simeq 10^{-6}$ second later

$$OH \ (A^2 \Sigma^+) \longrightarrow OH + h\nu_2 \ (3100 \ \mathring{A}) \ .$$

It can also be used to measure other atmospheric species such as : (8,9,10)

$$H_2O_2 + h\nu \ (\lambda < 1489 \ \mathring{A}) \longrightarrow OH \ (A^2 \ \Sigma^+) + H + O,$$

$$HNO_2 + h\nu \ (\lambda \simeq 1500 \ \mathring{A}) \longrightarrow OH \ (A^2 \ \Sigma^+) + NO_2 \ ,$$

$$NO_2 + h\nu \ (\lambda < 4000 \ \mathring{A}) \longrightarrow NO \ (A^2 \ \Sigma^+) + O \ .$$

3. THE MATERIAL

There are four atmospheric parameters that we consider as being the most important for the selection of the material that will protect the miniature photon countin detector:

- humidity
- temperature
- pressure
- weight.

For a stratospheric instrument, humidity results from water vapor and water accumulation during the balloon ascent when it crosses low altitude atmospheric clouds resulting either in the contamination of the measurements or in some cases in the destruction of the whole experience. This kind of contamination and the one produced by the outgassing coming from different parts and materials from which the entire system has been built have been the main or direct reasons to accomplish the atmospheric research using long duration atmospheric ballooning, hence it is well known (2) that most of the contamination problem will be overpassed if the system has the time to eliminate all the unwanted outgassed molecules in the stratosphere before the measurements start to be taken. At the same time as the experience in launched at ground level it will have to suffer a severe temperature gradient before reaching its floating altitude hours leter, which means that all the active and passive elements that constitute the instrument and that were manufactured with divers electrical and electronic tolerances must be capable to resist and operate under atmospheric enviroments where the temperature may attain -80°C as shown on Fig. 2.

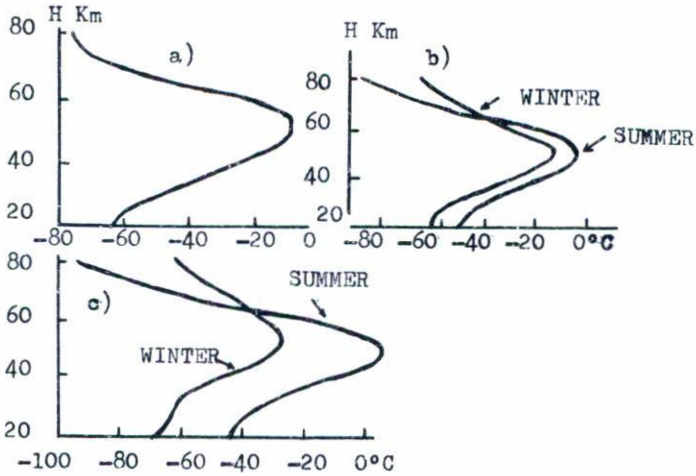

Fig. 2 Mean annual temperature at 15° latitude (a); temperature for the latitudes of 45° (b) and 75° (c).

The pressure problem arises in stratospheric research instruments when for the molecular photodissociation of minor species the applied method uses high voltages to bias photomultiplier tubes or ultraviolet radiation lamps that can be self-destroyed by an arc and gas ionization phenomena that occur over a pressure margin or window from 25 to 1 mb, called the forbidden pressure zone. Up to, this for short duration balloon flights, this breakdown problem has been solved by the aid of pressurised stainless steel containers, which represent a significant weight contribution for *in-situ* measurements but without importance for vertical stratospheric excursions of less than 15 hours. However, for long duration flights all the conventional ballooning methods had to be reconsidered and a high degree of miniaturization and weight reduction had to be obtained.

A new solution to replace the containers had to be found to avoid at the same time the gas ionization and arc phenomena, knowing that the total weight of the instrument that integrates the photon counting detector should not surpass 10 kg, according with the new CNES* regulations for long duration stratospheric flights. All these arguments and atmospheric parameters require a space tecnology solution where primer substances that bond metallic and non-metallic materials are extensively used to replace screws, bolts, rivets, etc., representing a spectacular reduction of weight and costs. In Table I we give a list of some of the space vehicles that were fully analyzed and we can see that besides the common metals used in their construction, a group of synthetic polymers such as epoxies, urethanes, silicones and others which offered possibilities to solve our problems appears. By experience it is well known that epoxies and urethanes damage any measurement instrument at low temperature due to the high flexural strenght; however, there is a material that surpasses the others because it seems capable to bond glass and metals, semiconductors or solar cells to polymers and metallic materials and that can support very hight temperature gradients, with good outgassing and dielectric characteristics. This material is silicone, a synthetic elastomer whose main characteristics are:

- Excellent behavior under high temperature gradients (-100 to + 800°C)
- Resistance to the ultraviolet radiation
- Chemical inactivity
- Compatibility for electronic applications
- High dielectric strenght in Kv/mm
- Excellent arc resistance
- Silicon properties remain constant under high vacuum conditions.

Some of these properties are graphically shown on Figs. 3, 4 and 5. Besides these characteristics we can say it is an inorganic and organic elastomer that belongs to a group of synthetic polymers. Having

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* Centre National d'Estudes Spatiales

a quartz type lattice alternating silicone and oxygen atoms as follows:

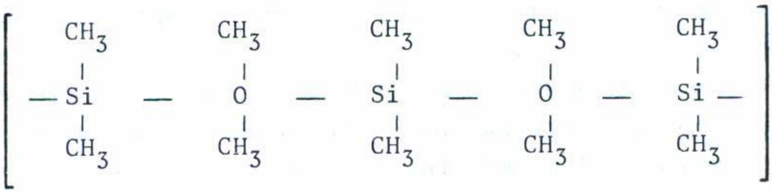

TABLE I

SPACECRAFT	ADHESIF	APPLICATION
EXPLORER	Base epoxy and silicon RTV	Solar cells bonding, silicium cubes fixed in aluminium
NIMBUS	Silicone RTV	Camera optics bonding, TV target bonding
PIONEER	Epoxy, silicone RTV	Solar cells bonding
RANGER	Epoxy, silicone RTV	Solar cells bonding to mylar
SURVEYOR	Epoxy, silicone RTV	Mirror bonding, solar cells bonding
APOLLO	Epoxy, silicone RTV	Glass windows bonding, solar cells bonding, measurement instruments building

Table I. Some common synthetic materials used in spacecraft building.

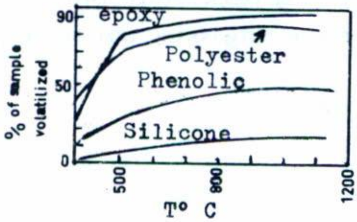

Fig. 3 Thermal stability for a group of plastic materials.

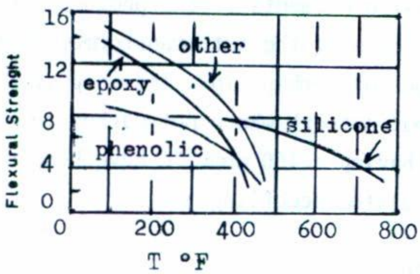

Fig. 4 Temperature effects for some RTV compounds.

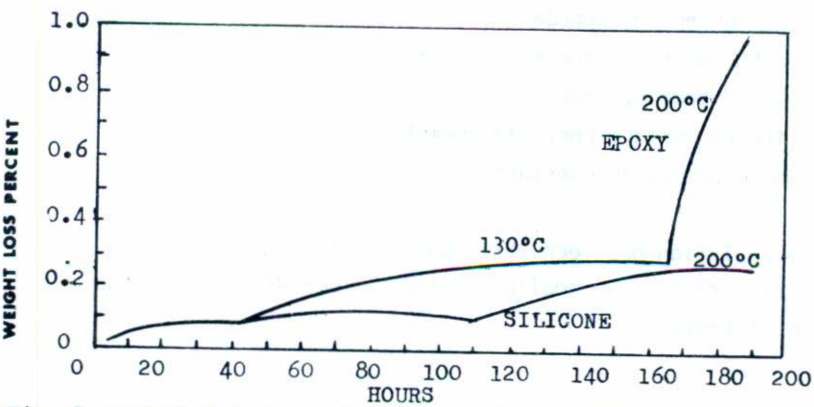

Fig. 5 Weight loss percent for several RTV compounds.

This molecular structure makes this kind of materials easy to mould and unmould according to the required applications. They can be polymerized in several ways, either by room temperature vulcanization or by very high temperatures, improving their outgassing and space properties.

4. RESULTS

a.- Photon counting detector

A total gain variation of the order of 8% in all the temperature range from + 40 to -80°C can be estimated for the photon counting set. This variation is atributed to a high voltage biasing drop from 1000 dcv at room temperature to -985 dcv at -80°C that is produced by the efficiency change of the miniature passive elements of the photomultiplier power supply, such as the magnetic core of the autotransformer that changes the oscillating pulse shape and perhaps in a less significant contribution to the filterinf output network where polycarbonate capacitors and high quality resistors having a 100 ppmv/°C have been used. This gain variation has been calculated according to

$$G = (AE^{\alpha})^{n} = KV^{\alpha n},$$

where:

n - the number of dynodes
α - a PM constant from 0.7 to 0.8
E - the dynode voltage
V - the PM voltage operating point
A - a PM geometric constant.

This variation has been obtained with the test array shown on Fig. 6 after several sistematic cooling periods from + 40 to -80°C that lasted 8, 24 and 48 hours.

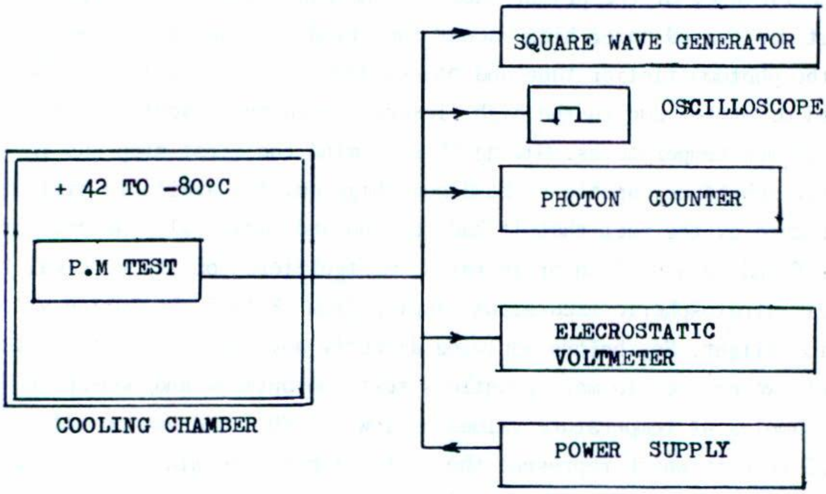

Fig. 6. Low temperature and test array for the photon counter detector.

The frecuency limit of the preamplifier and amplifier chain can be of only 110 khz or 1.1 x 10^4 counts/sec at room temperature but we can see that the frequency behavior of the chain is gradually improved as the temperature decreases with the pulse with changing from 4μ sec at + 40°C to 2.6 μ sec at -80°C. At the same time the darkness current values for the same temperature gradient are radically improved from ∿ 100 counts per second at room temperature to 1 ± 1 counts per seconds at the lowest temperature value.

b - Silicon bonding

For quite a long time bonding of a material around the glass body of a photomultiplier tube has been the main problem of space technology workers at the Service d'Aeronomie du CNRS in France. Many synthetic materials had been tried out in order to protect its vital biased parts against troposhperic and stratospheric humidity when it was outside a pressuriezed container. In every case it was damaged, either by the deterioration of the bonding materials with time at low temperatures or by the unefficiency of the primer used to bond glass-synthetic materials when it was tested under high vacuum conditions. Frequently it was found that the photomultiplier tube and associated counting electronics had been cracked or broken due to the high flexural strength presented by the mate rials at low temperatures. Having this in mind the first step was to get a primer substance capable to bond some high quality available silicones, conditioned by the fact that it had to keep and resist all the pressure values found by a balloon or infrared "montgolfiere" on its vertical trop ospheric-stratospheric excursions ranging from 18 to 31 km during a long duration flight. So, before applying directly any silicone compound to the set, we proceed to make countless tests on optical and non-optical glass samples at temperature values as low as -80°C and vaccum values from 25 to 6 mb which represent the critical pressure window for research instruments out of a metallic container. We show in Table II the primer substances and silicone code numers that satisfied these temperature and pressure requirements over time periods of 8, 24 and 48 hours. We think that the success of these results is due to the combination of primer sub stances and silicone products coming from different manufactures.

TABLE II

PRIMER SUBSTANCES		SILICONES	
		ECC 1776	(1)
MB	(2)	ECC 4954	"
4094	(1)	ECC 4966	"
1.- Emerson and Cuming.		ECC 4122	"
2.- Rhone Poulanc.		ECC 2N	"
		RHOD 141	(2)
		RHOD 148	"

Table II Primer substances and silicones for stratospheric research instruments.

In Table II some of the silicones are transparent while others are not; however, for the final selection we took into consideration those that could offer a minimal weight or those with a minimal specific gravity. From this list the ECC 4954, appearing as a classified NASA product, presents the lowest TML and CVCM porcentage. This quality makes this compound very suitable for our case and in the same way the ECC 4122 guarantees low outgassing and an important light opacity. The physical representation of the miniaturized prototype is shown on Fig. 6, where we can see that the primer substance MB that sticks the silicone to the PM glass body has been applied ≃ 5 cm appart from the quartz window, but far enough from the pin electrodes, avoiding an arc path formation between these and the external atmospheric air. After that two or three thin layers of silicone ECC 4954 with a 20 KV/mm dielectric strenght are successively overlapped using the necessary space technology methods with a vulcanization period at a temperature of 42°C, during 15 hours for each layer. The rest of the photon counting elements are added to the photomultiplier and in this way the process to mold the new stratospheric container using the silicone ECC 4122 can be started. The dimensions of the new container as shown on Fig. 7 are 4.4 cm in diameter and ≃ 20 cm lenghth, weighting, no more than 250 gr. For a better protection this synthetic cylinder will be introduced in a very light 1 mm thickness cylinder during the flight.

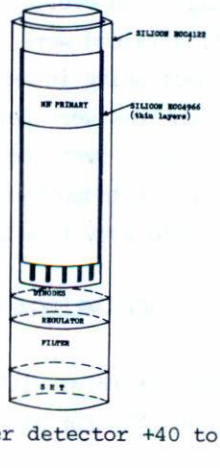

Fig. 7 Miniature photon counter detector +40 to -80°C; 2 mb pressure.

c.- Vacuum results

Several vacuum tests were done to the laboratory prototypes and final photon detector. These allowed us to study the behavior with time and vacuum of the silicone and primer bonding. Some of these tests never went further than 5 and 1 mb of pressure during 6 and 12 hour periods. However, others with high vaccum values of 10^{-8} torr were also performed during the same periods in several vacuum sessions.

The observed results were quite satisfactory and no damage was detected in the bonding. Although the cool and vacuum tests were done in a separated way, we think that they gave us a general idea of what will be the behavior of the photon-counter when it will work under all the combined atmospheric conditions. However, we know that after the author left the Service d'Aeronomie, simultaneous tests were done in a new vacuum-cooling Secasi chamber which are in agreement with the earlier results. After these passive state tests, we had to consider the pressure changes that the instrument could find during the balloon ascent. That means that we have to produce pressure changes following the next sequence: 70 mb pressure steps which are the variations per kilometer during the first 10 kilometers of balloon ascent, 24 mb pressure changes for the next 10 km and finally 2 mb steps corresponding to those atmospheric changes from 20 to 30 km high. In every one of the three test sequences the minimum pressure limits attained were of 5, 3 and 1 mb keeping the photon counting detector functioning in an active saturation mode during 5 hours and no ionization problems were perceived. The model that we have shown in Fig. 7 is able to work over the required pressure and cold conditions for long duration stratospheric flights where the night and day balloon oscillations [11] could vary from 18 to 32 km high.

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