The Ubiquitous Nature and Objectionable Characteristics of Phthalate Esters In Aerospace Technology

by Frederick C. Gross* and Joe A. Colony*

Building a spacecraft and equipping it with a variety of sophisticated experiments is no easy task. Planning for a launch may begin five years or more in advance. Thousands of specialists take an active role in the planning, design, fabrication, testing, checkout, launch, and data-handling phase of the project. Parts of the structure, if not entire experiments, are designed and produced all over the world even though the project may belong to one country in name.

With a task of this magnitude it may plainly be seen that it is impossible to control completely every procedure, environment, or material associated with a project. Each succeeding program naturally strives to refine the data of a previously successful flight. To do this, the state-of-the-art must be advanced, which usually means adding a digit or two to the right of the decimal. As with any other science, this is much more easily said than done. Frequently, the accomplishment of these goals may depend heavily on the chemical and/or physicochemical properties of the system.

Many, if not most, space experiments are of an optical, thermal, or physical chemical nature. To be accurate and meaningful these data must be collected at well defined conditions or, in other words, with a minimum of the interference caused by contamination. Although particulate contamination is of no little concern, the danger of the greatest detriment to the experimental measurements is from volatile (mainly organic) contaminants at spaceflight conditions.

Spaceflight parameters characteristically may consist of: (1) continuous temperature cycling from -40 to 50°C but at times as high as 200°C; (2) pressures as low as 10^{-8} to 10^{-12} mm Hg or even less; (3) constant exposure to ultraviolet and other types of radiation; (4) during launch a combination of high *g* forces and vibration.

It is the combination of the temperature and reduced pressure that set the stage for molecular contamination of critical experiments.

Aerospace experiments are self-contaminating as well as being contaminated by their environment. The principal sources of self-contamination are: potting compounds, conformal coatings, paints, lubricants, adhesives, and structural polymers. Sources of environmental contamination may be somewhat less obvious but in some cases much more serious because of their insidious nature. A few of the most common sources of environmental contaminants have been improper air circulation systems, dirty

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or poorly fabricated vacuum systems, unapproved or contaminated solvents and containers, purging gas systems, and "protective" covers and containers.

Since plasticized poly (vinyl chlorides) are not allowed in the materials lists of spacecraft, and, in fact, the use of any plasticized polymer is strongly discouraged, one would hopefully not find the usual plasticizers vaporizing in thermal vacuum testing. In the aerospace jargon we refer to this release of volatile constituents during testing and flight as outgassing. In truth, this outgassing always takes place, but in varying degrees depending on the conditions of the test and how much care was taken in cleaning, choice of materials, and handling techniques. The compounds that escape are to some extent representative of the basic organic materials used in fabrication. Much too often, however, we see common plasticizers that are not representative of the basic materials used in fabrication. In the majority of these cases the plasticizers are PAEs, and of those the most common is DEHP, which follows along closely with the production figures *(1)* (Table 1).

It has not always been possible to isolate the source of PAE contamination, since some of the history of space hardware is obscured either by incomplete recordkeeping or by design. In the cases where sources of contamination have been established, the following are representative examples: (1) contaminated wash solvents by the use of PVC containers, cap liners, or PVC tubing for transfer of the liquid; (2) use of vinyl gloves for handling critical experiments such as optics; (3) use of PVC tubing for purging optics or other sensitive packages, also for transfer of gases to tanks and experiments needing a pressurized or inert atmosphere; (4) Use of DEHP (DOP) for treating filters to be employed in clean rooms; (5) use of PVC sheets, bags, or tents for "protection" of space hardware in storage or shipping (vinyl strippable coatings also being used); (6) from a variety of aerosol products in which the PAE served no functional purpose but was present in significant quantities presumably as a contaminant; (7) from vinyl tapes and tape adhesives containing the PAE; (8) from wire insulation; (9) from alkyd paints erroneously used on spacecraft and inside vacuum chambers; (10) from dirty vacuum systems and systems using Octoil as the pump fluid.

It is not the intent to imply that PAEs are the only contaminants that cause consternation. There are some annoying problems caused by the frequent appearance of a variety of aliphatic hydrocarbons, silicones, and aliphatic esters, but many of these can either be tolerated, minimized, or at least explained on the basis of known materials present.

Several years ago Frissel *(2)* showed the considerable volatility losses of some common plasticizers when processed in a standard milling test in conjunction with a mixture of 95% vinyl chloride and 5% vinyl acetate at 170°C (Table 2).

Although most spacecraft do not ordinarily operate at such an elevated temperature in test or flight, they do experience pressures as low as 10^{-7} mm in test and much

Table 1. U.S. production and value of plasticizers: 1967–1969.

Material	Production, 10^6lb			Sales value, 10^6 $		
	1967	1968	1969	1967	1968	1969
Total of all plasticizers	1262	1331	1382	261	280	265
Phthalic anhydride esters, total	784	841	884	125	133	127
Di-2-ethylhexyl phthalate	293	330	355	43	49	45
Diisodecyl phthalate	123	137	137	18	20	18
Diisooctyl phthalate	98	94	83	16	13	13

Table 2. Plasticizer loss in milling test at 170°C.

Plasticizer	Rate, $g/m^2/min$	Loss, %/hr
n-Octyl *n*-decyl phthalate	0.5	1.4
Di-2-ethylhexyl phthalate	1.0	2.8
Tri-2-ethylhexyl phosphate	1.2	3.4
Di-*n*-hexyl phthalate	1.3	3.7
Di-2-ethylhexyl adipate	1.8	5.1

lower levels in flight for extended periods of up to several years at average temperatures of 25–40°C. The temperature–vapor pressure relationships of several common plasticizers shown in Table 3 would be very significant when translated to test and, especially, flight conditions. Most of these compounds or some closely related ones have been detected in flight-preparedness vacuum testing of spacecraft.

Table 3. Temperature–vapor pressure data for some common plasticizers.

Plasticizer	Temperature, °C, at vapor pressures of 5×10^{-8} mm Hg	5×10^{-6} mm Hg
Di-2-ethylhexyl sebacate	84	131
Di-*n*-octyl phthalate	82	132
n-Octyl *n*-decyl phthalate	80	138
Tricresyl phosphate	78	136
Diisooctyl phthalate	72	121
Di-2-ethylhexyl phthalate	68	120
Di-2-ethylhexyl adipate	58	105
Tri-2-ethylhexyl phosphate	57	110
Di-*n*-hexyl phthalate	54	120

Because we must accept the realities of outgassing, which at best, has only been minimized through materials selection and proper cleaning procedures, it is very urgent to the success of the programs that we compensate for this phenomenon. To do this properly, it is necessary to understand the mechanisms of deposition and desorption.

An interesting study by Baurer and his associates *(3)* to determine the various factors that influence surface deposition of contaminants has been performed. A few of the most significant findings of this study are as follows.

(1) Gaseous contaminant transport depends on gas/surface interaction potentials and hydrodynamic, electrostatic, and magnetic fields.

(2) Condensed phase materials are subject to hydrodynamic coupling, induced polarization, and electrostatic field effects.

(3) The nature of the surface is either conducting or dielectric with the dielectric preferentially attracting more of the contaminants.

In another significant and related experiment by Tominaga *(4)*, a careful study was made of the desorption rate of contaminated surfaces, considering such materials as common esters, hydrocarbons, and silicones used as diffusion pump fluids. It is also noteworthy to relate that these same esters are also used as plasticizers and one is the omni-present DEHP, sometimes referred to as Octoil, as in this instance.

The major findings of this experiment were that "oil molecules impinging on a clean glass surface are assumed to be absorbed with a fairly large desorption energy such that their sojourn time is considerably longer. Such adsorbed oil molecules can scarcely be desorbed by reducing the vapor pressure over the surface and can only be desorbed when the temperature of the adsorbent is increased. However, further adsorption takes place with a desorption energy which is nearly equal to the latent heat of vaporization."

An illustration of the determination of this principle is shown by the two curves of Figure 1. In curve *(a)* the characteristics of an ultracleaned surface are demonstrated. Curve *(b)* is representative of a surface that

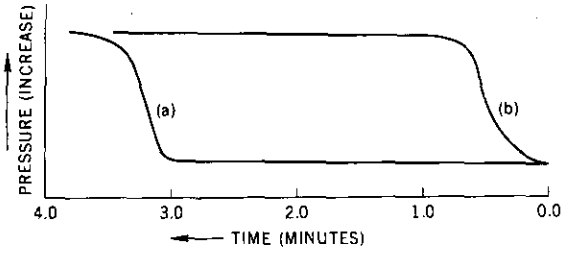

FIGURE 1. Flow rate of DEHP vapor at 75°C: *(a)* first flow of DEHP through ultraclean glass tube; *(b)* second and subsequent flows through same tube after *(a)*.

has already been saturated with DEHP and depicts second and subsequent absorptions and desorptions from this surface.

The implications of these phenomena are quite significant in the theory and solution of our problems. More specifically, for instance, it is known from experimentation that all surfaces of a spacecraft do collect outgassing and other contaminants that are characteristic of the historical environment of the hardware involved. From the surface absorption–desorption studies, calculations can be made to determine the conditions necessary to remove the bulk of surface contamination except for a monolayer or so that will remain unless rather severe conditions are used for removal. In most cases total removal of the contaminant would not be necessary; in fact, many surfaces have been coated purposely for one reason or another. Working with surfaces containing this ultrathin layer of contaminant is standard, and calculations usually include this parameter.

Ultraviolet optical equipment is particularly vulnerable to contamination and degradation. Some very interesting experiments by Gillette and Kenyon *(5)* have been performed on LiF/Al-, MgF_2/Al-, and Pt-mirror surfaces to illustrate this effect. Proton irradiation was used to induce deposition of contaminant film on the optical equipment, which was more markedly affected in some cases in the vacuum ultraviolet range. This is particularly important because some satellite experiments are using these optics in this same spectral range.

Note in Figures 2, 3, and 4 how the reflectances of MgF_2/Al-, LiF/Al-, and Pt-coated glass diminish when a 4–5 nm thick oil film is deposited on them by using proton-induced deposition (1 x 10^{16} protons/cm^2). The MgF_2 and LiF reflectances are affected in a wavelength-dependent manner, whereas the Pt reflectance is almost uniformly affected throughout the measured spectral range. An interferometer was used to measure the film thickness of the deposited contaminant oil. Although no chemical analysis was made to determine the molecular species of the oil present, it may probably be safely assumed that the contaminant was a combination of pump oil and various chamber contaminants.

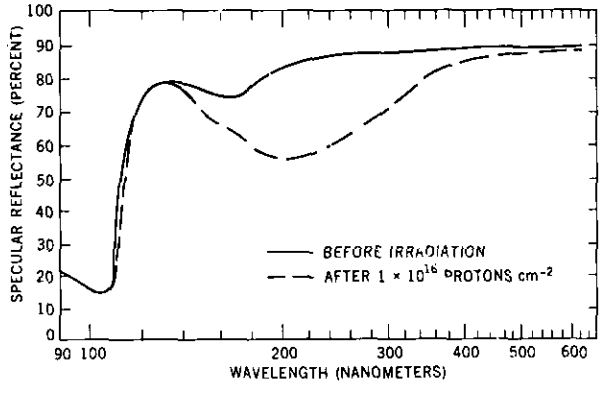

FIGURE 2. Reflectance changes of a MgF_2/Al-coated CER-VIT mirror resulting from deposition of contaminant film during proton irradiation (MgF_2 thickness of 25 nm).

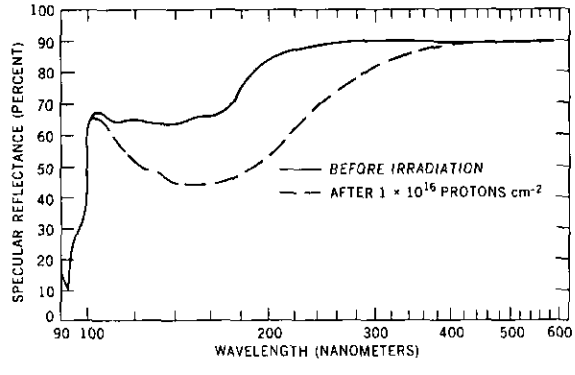

FIGURE 3. Reflectance changes of a LiF/Al-coated fused silica mirror resulting from deposition of contaminant film during proton irradiation (LiF thickness of 14 nm).

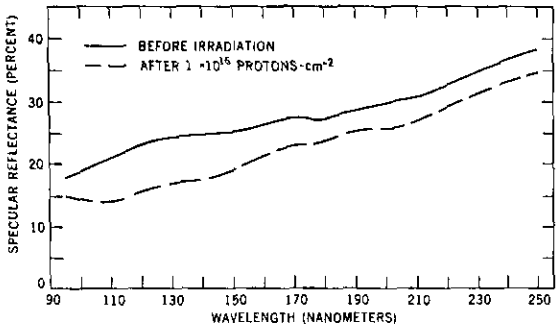

FIGURE 4. Reflectance changes of a Pt-coated glass mirror resulting from deposition of contaminant film during proton irradiation (Pt thickness about 10 nm).

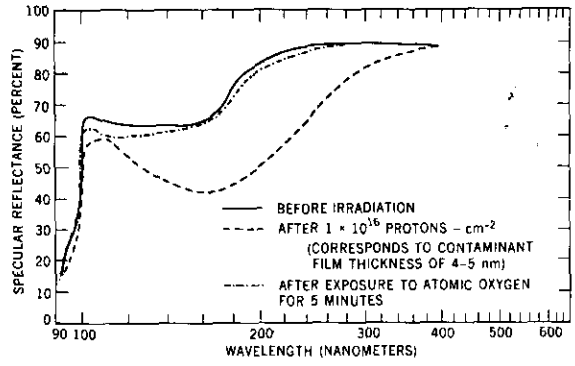

FIGURE 5. Reflectance recovery of a contaminated LiF/Al-coated fused silica mirror exposed to atomic oxygen.

It would not be unreasonable to assume that most thin oil films would react similarly in this region of the spectrum. At GSFC it has been shown that similar polymerization of vacuum chamber contaminants also occurs on surfaces irradiated with either ultraviolet or high-energy electrons. Questions were raised as to how easily this radiation-induced oil film might be removed and whether the radiation had permanently changed the optical properties of the mirrors. As a result, several cleaning methods, including Freon and collodion, CCl_4 soaking, and $CaCO_3$ abrasion, were attempted to see what form the oil had taken and how best to remove it. None of these methods was satisfactory, mainly because the oil had polymerized and probably crosslinked. Thus, it had become impervious to the solvents and $CaCO_3$ was too harsh for the mirror coatings. Finally, the mirrors were exposed to atomic oxygen for 5 min; the result was almost complete recovery to the original condition (Fig. 5). This was a rather interesting discovery, because it showed that the mirror surface itself was changed to a rather minor degree as a result of the proton irradiation and also that the contaminant could be easily removed without damaging the mirror surface. Incidentally, it was concluded that the slight final change experienced by the mirror was caused by a minute reduction in the LiF thickness. These experiments have taught us that a relatively good vacuum (10^{-6} -10^{-7} mm Hg) should be obtained before irradiating a spacecraft or piece of hardware in test to prevent polymerization of contaminants on the surface.

Experimental Methods

A variety of methods (Fig. 6) is being used to determine the extent and nature of prelaunch spacecraft contamination. These include *in situ* residual gas analysis (RGA) and quartz crystal microbalance measurements during vacuum testing. After test completion, contamination areas are sampled, followed by infrared analysis of the residues, ultraviolet vacuum monochrometer measurements of test mirrors placed in strategic areas of the chamber, and collection of outgassing condensates on liquid-N_2-cooled condenser plates that have been installed in the vacuum chambers. These condensates are then subjected to a chemical analysis, the extent of which is based on the particular situation. It is this latter procedure that has been proven most useful, because the condensable outgassed materials that are potentially most harmful to the mission are collected in quantity. The analytical procedures necessary for identification include gas and liquid chromotography in addition to infrared spectroscopy and mass spectrometry, which are described in more detail later in this report.

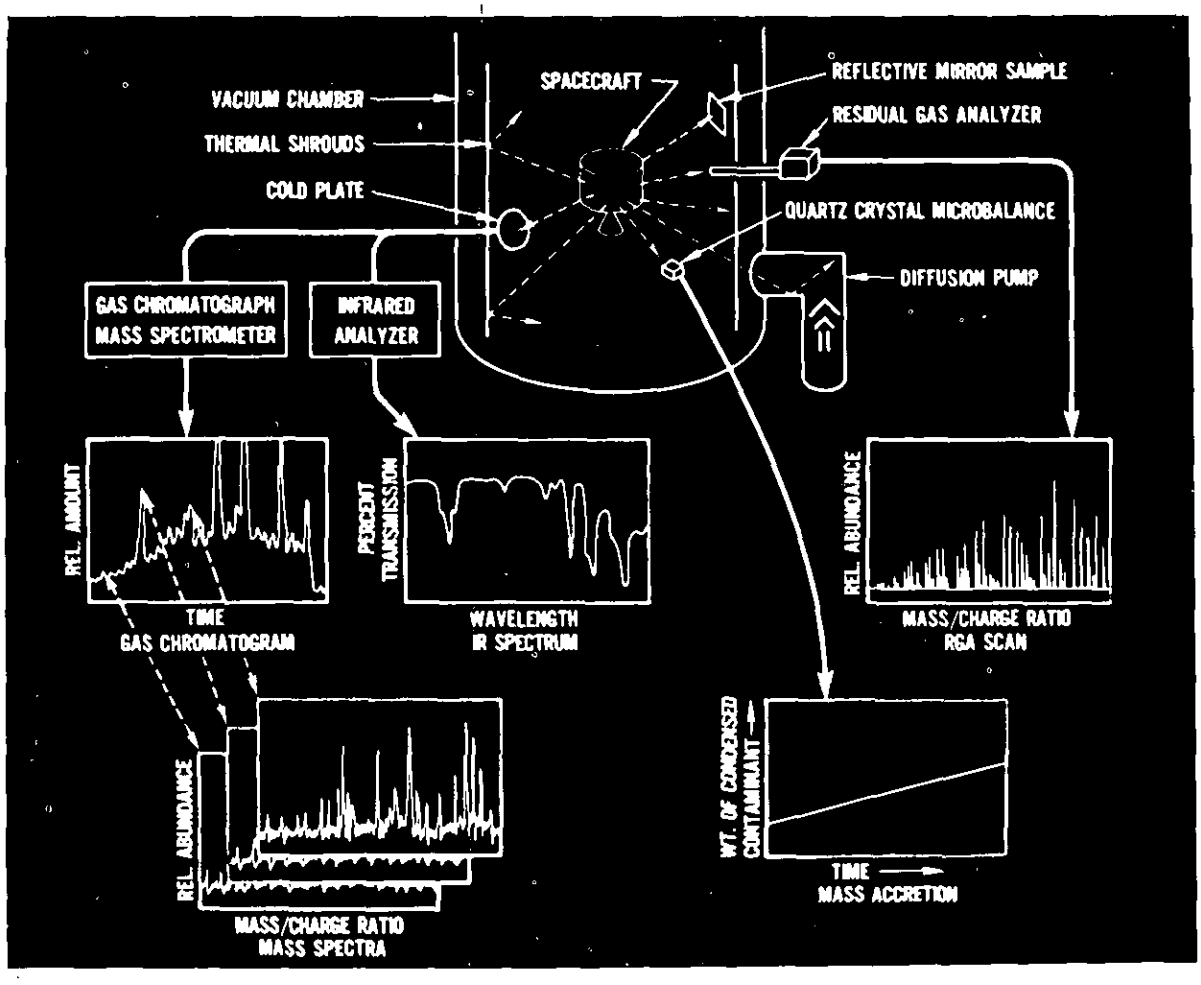

FIGURE 6. Relationship of measurement methods.

The amount of material collected on a cold finger during thermal vacuum testing of a spacecraft may be as much as several grams and generally consists of three classes of compounds; namely, esters, silicones, and hydrocarbons, with occasional traces of fatty acids and other human outgassing products. Although separation of components reveals as many as 80 to 90 or perhaps even more distinct compounds in a sample, the most ubiquitous of the lot are the phthalate esters. As previously mentioned, a rather subtle source of phthalate contamination is produced from high-efficiency particle filters known as HEPA filters used in cleanroom and similar type air purification systems (Fig. 7) where the entire cleanroom wall is made-up of these filters. The phthalate ester, usually DEHP, is sprayed as a 0.3μm smoke on the back side of these filters to check their efficiency in removing this size particle. Even though the ester does not emerge immediately and, thus, the filter is considered satisfactory, there is good evidence to show it will diffuse through the filter over a period of time and is eventually carried into the cleanroom or wherever the air is being delivered to be subsequently deposited as a thin film on all exposed surfaces. As a result, it is always recommended that critical optics, detectors, and other sensitive equipment be exposed in the cleanroom atmosphere for the minimum time to accomplish a specific task. Modes of

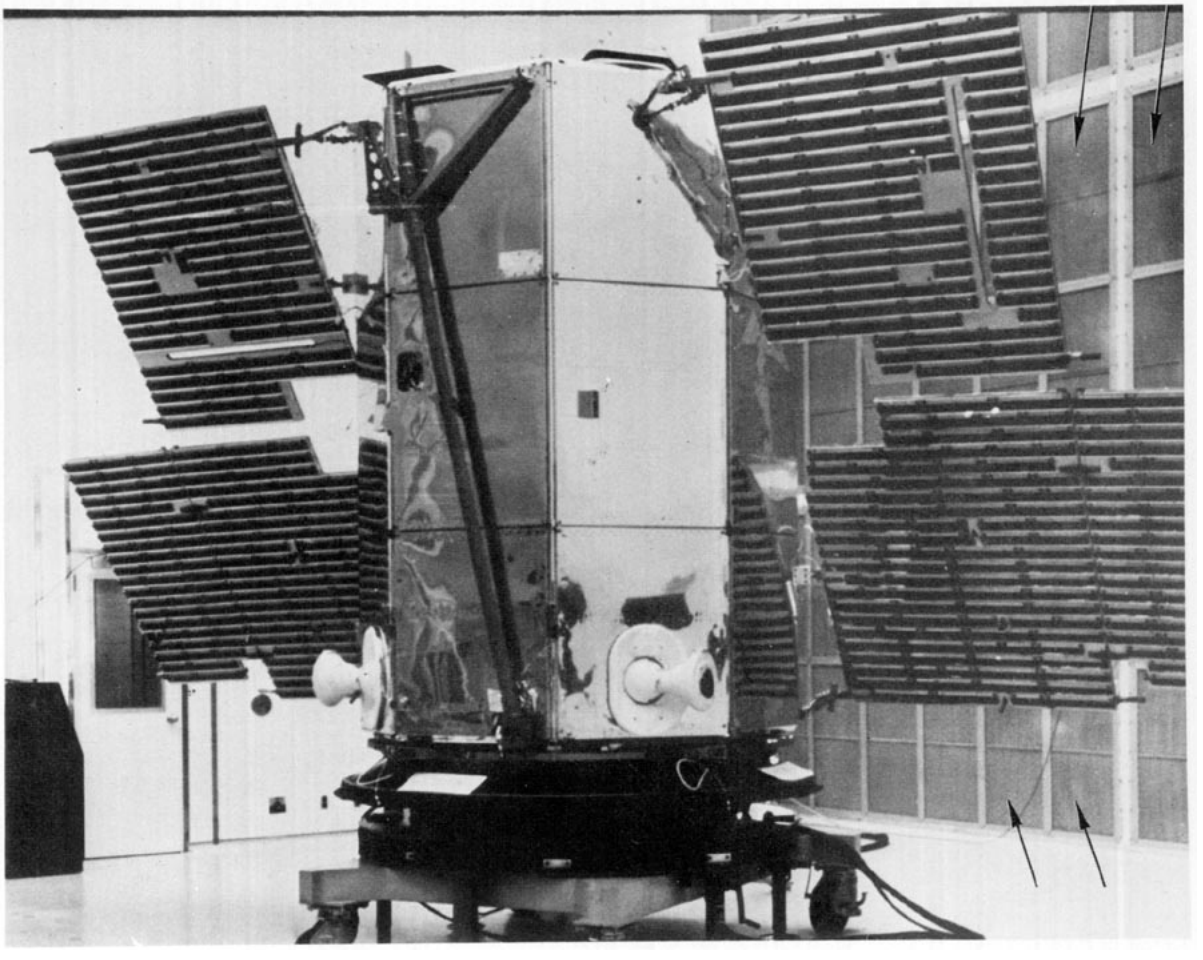

FIGURE 7. HEPA filters in clean room walls.

distribution of the phthalates and other related plasticizers include creep along surfaces, solvent extraction and redistribution, contact transfer, and vaporization followed by condensation processes caused by significant vapor pressures of the different esters at characteristic test temperatures and reduced pressures.

Analyses of Outgassing Residues

Spacecraft 1, although built by NASA, carried 28 experiment modules assembled by various universities and research centers around the country. Some of these experiment modules were available for individual thermal-vacuum testing but most were not; and because of the diversity of the sources of the hardware, little control of material selection from an outgassing point of view was possible. Thus, it was not surprising that a copious amount of condensable material was collected on the liquid-N_2-cooled condenser plate during thermal-vacuum testing. In fact, this amount of material was so disconcerting to project managers and experimenters that five or six extensive thermal-vacuum soaks were performed to reduce the potential amount of outgassing material before launch. Infrared spectroscopy of each of these samples showed that although the amount of outgassed material was reduced, its composition remained quite constant, consisting mainly of esters, silicones, and high molecular weight hydrocarbons as shown in Figure 8. Our primary means of

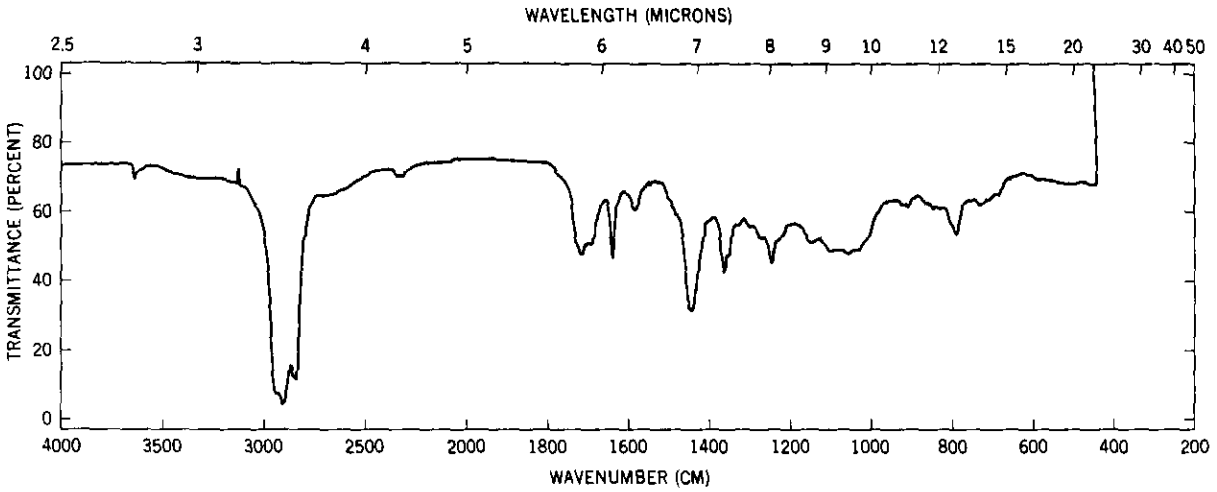

FIGURE 8. Infrared spectrum of spacecraft 1 cold- plate condensables.

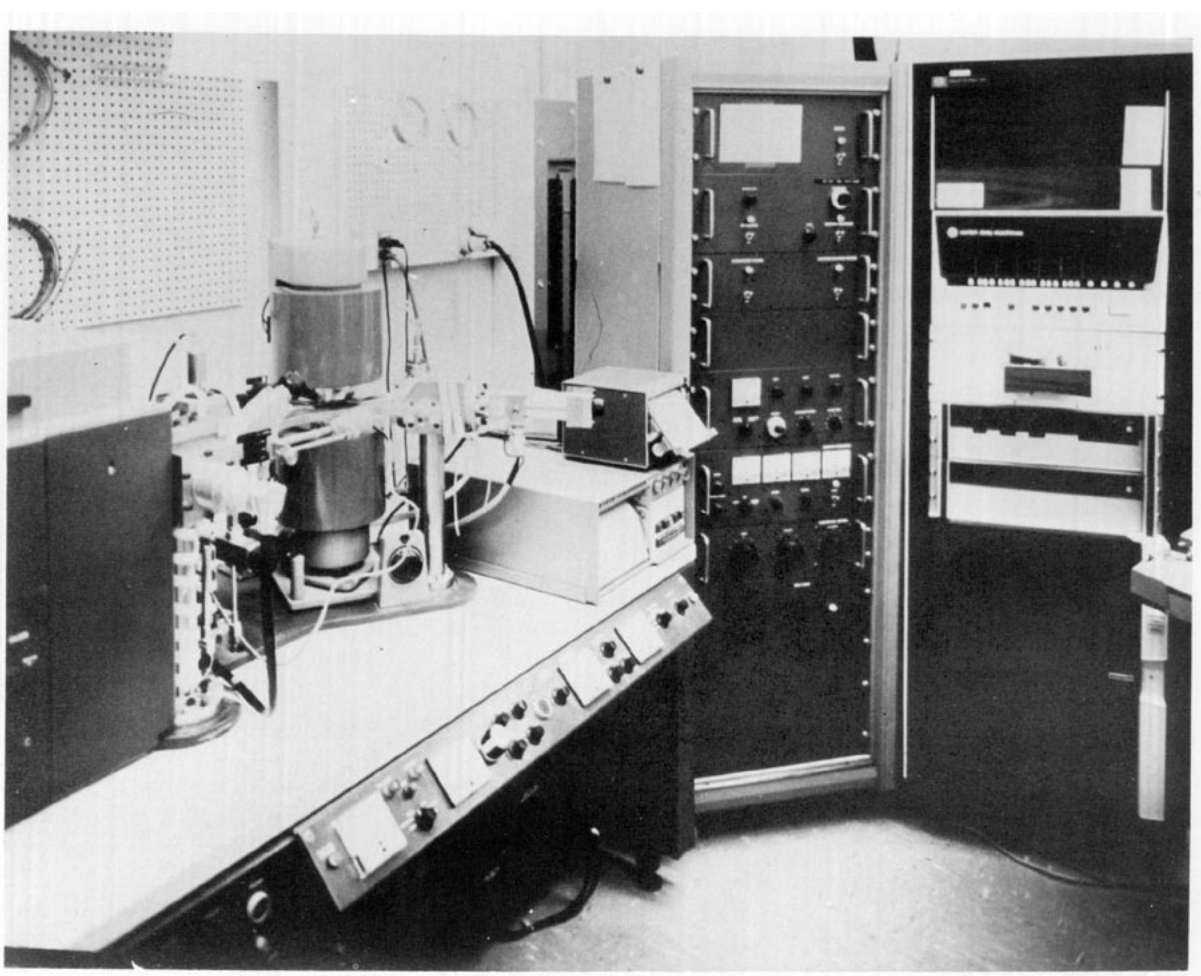

FIGURE 9. Computerized gas chromatography/mass spectrometry system for identification of contaminants.

specific identification of compounds was by combined gas chromatography/mass spectrometry with a computer interface (Fig. 9) and readout of mass lists and relative abundances by teletypewriter, a typical example of which is the DEHP spectra shown in Figure 10. Analysis of the raw outgassing mixtures from Spacecraft 1 produced the poor chromatogram shown in Figure 11. Although DEHP was identified from this separation, it was apparent that the large unresolved background of hydrocarbons would obscure further identification. To eliminate this problem the crude outgassing mixture was first subjected to a simple liquid chromatographic separation with the use of isooctane followed by chloroform elution through a silica gel column. The separated fractions were again subjected to the gas chromatography/mass spectrometry procedure with somewhat more gratifying results. First, the isooctane fraction (Fig. 12) contained most of the hydrocarbons (still unresolved) as well as two fumaric acid esters. More polar materials, including a large

MASS LIST
COMPUTER PRESENTATION

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01 MTR, 470,
02 MASCON
03 MTW
04 SUB, 470, 469,
05 MLIST
06
RUN
BACKGRND PEAKS MISSING
PEAKS BCKGRND    70
6/1/71  /SPEC#  486/LM/
  BASE          SUM
  29031        248730
```

PEAK	INT	I/BASE	MASS	TEST
1	1466	5.04%	18	-1
3	2722	9.37%	27	-2
4	1730	5.95%	28	-2
5	6940	23.90%	29	-1
7	2499	8.60%	39	-2
9	12853	44.27%	41	-1
10	3405	11.72%	42	-1
11	14850	51.15%	43	-1
12	13404	46.17%	55	-1
17	5312	18.29%	56	-1
18	19597	67.50%	57	-3
19	1909	6.57%	68	-1
23	18904	65.11%	69	-0
24	15749	54.24%	70	0
25	3048	10.49%	75	3
28	4434	15.27%	83	-0
33	5227	18.00%	104	-1
39	5669	19.52%	112	-0
45	7904	27.22%	113	-0
46	29031	100.00%	149	-0
60	8852	30.49%	150	-0
61	21882	75.37%	167	-0
63	2499	8.60%	168	-0
75	3453	11.89%	279	0

FIGURE 10. DEHP mass list, computer/teletype presentation.

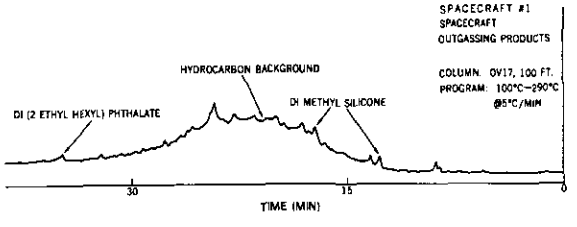

FIGURE 11. Spacecraft 1 outgassing products. Column length, 100 ft (SCOT); liquid phase, OV-17; program, 100—290°C at 5°C/min.

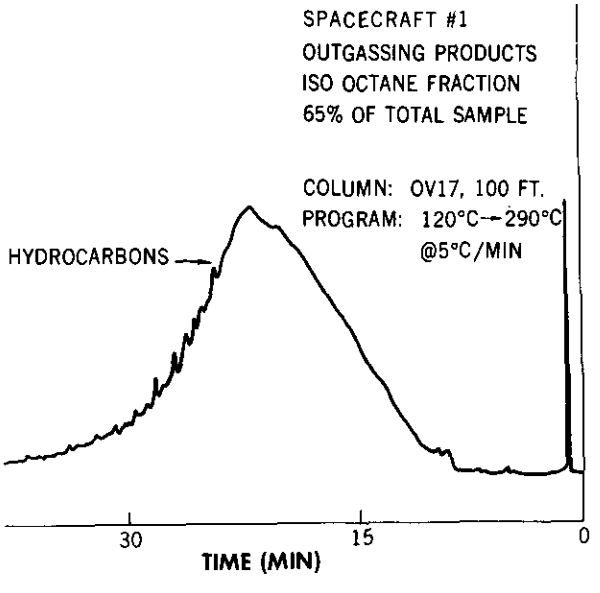

FIGURE 12. Isooctane fraction of Spacecraft 1 outgassing (contains 65% of total sample).

number of silicones and DEHP, were contained in the first chloroform fraction (Fig. 13); the second chloroform fraction (Fig. 14) contained mostly esters of which only a few were definitely identified. Although these separations are somewhat crude and arbitrary, they do indicate the wide variety of volatile plasticizers that can be collected into an experimental package. Attempts to localize the sources of these materials were complicated by the inability to test experimental packages separately and the lack of complete materials lists. In the case of DEHP, the complication was that it was found to be an outgassing contaminant from all of the individual modules tested. Gas chromatograms of outgassing residues from three of these separate module tests are shown in Figures 15–17.

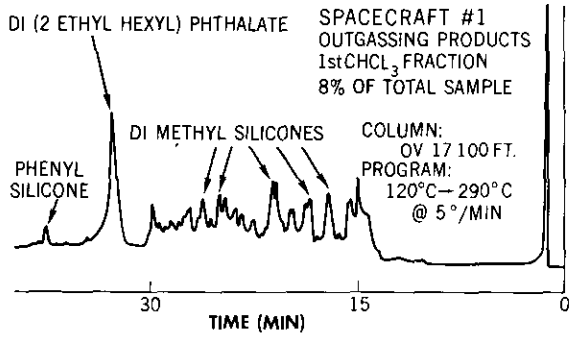

FIGURE 13. First chloroform fraction of Spacecraft 1 outgassing (contains 8% of total sample).

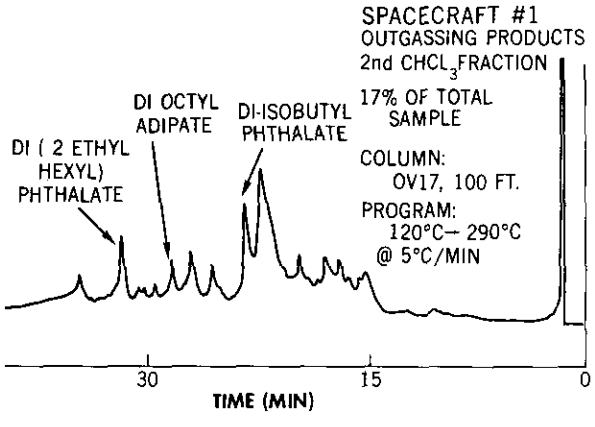

FIGURE 14. Second chloroform fraction of Spacecraft 1 (contains 17% of total sample).

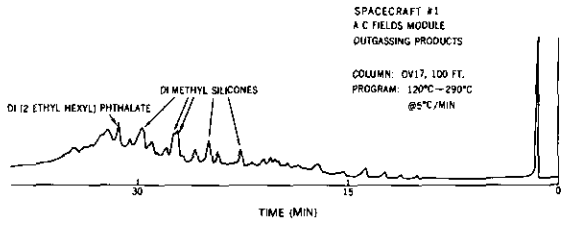

FIGURE 15. AC fields module of Spacecraft 1, outgassing products.

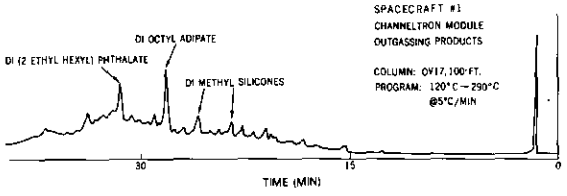

FIGURE 16. Channeltron module of Spacecraft 1, outgassing products.

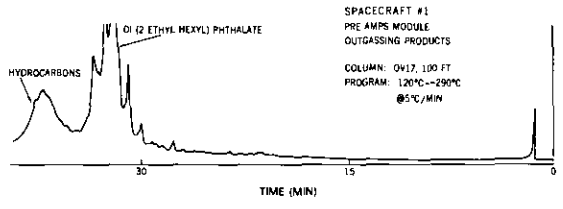

FIGURE 17. Pre amps module of Spacecraft 1, outgassing products.

Methylsilicone contamination seen in these outgassing residues is caused by the use of unapproved silicone cements and extensive silicone potting compounds for electronics. Examination of the spacecraft revealed that some of the hydrocarbons may have come from heavily waxed ties used to bundle electronic wiring, incompletely removed machining oil, and various greases. However, because the phthalate contamination emanates from nearly all parts of the spacecraft, it is apparent that future projects must be governed by more strict scrutiny of materials to eliminate, as nearly as possible, all plasticized compounds.

The ubiquitous nature of phthalates as a contaminating species on spacecraft is further demonstrated by similar analyses of outgassing residues from other projects. For example, Spacecraft 2 released large amounts of methylsilicones and DEHP (Fig. 18). A

dramatic example of phthalate outgassing was demonstrated by a module from Spacecraft 3 (Fig. 19) that produced an almost pure DEHP spectrum. Similar occurrences of phthalates have been observed in hundreds of samples, and, in spite of considerable effort toward controls, the frequency of appearance of phthalates remains somewhat constant.

Some very recent results in liquid chromatography have given us more hope in separating some of the most common contaminants by groups (Fig. 20) before subjecting them to the mass spectrometry/GC system.

One of the most meaningful pieces of information came to our attention a little unexpectedly. This consisted of a mirror from the television camera of the Surveyor III spacecraft (Fig. 21) which was on the Lunar surface for about 31 months. The mirror was returned by the Apollo 12 astronauts and washings and scrapings from the visibly affected surfaces were analyzed by mass spectrometry *(6)*. The results of the analyses indicated the presence of DEHP and several of the other common contaminants we have mentioned. This was a very significant finding, as many people previously

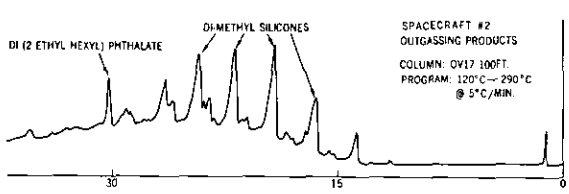

FIGURE 18. Spacecraft 2 outgassing products. Column length, 100 ft. (SCOT); liquid phase, OV-17; program, 100—290°C at 5°C/min.

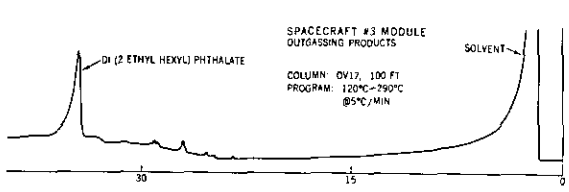

FIGURE 19. Spacecraft 3 module outgassing products. Column length, 100 ft (SCOT); liquid phase, OV-17; program, 100—290°C at 5°C/min.

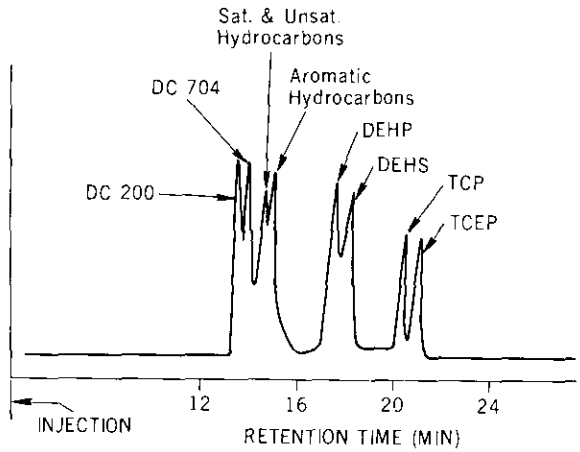

FIGURE 20. Liquid chromatogram showing separation of some typical spacecraft contaminants. Column, Corasil II, 6 ft; solvent, 8% C_2H_5OH in 2,2,4-trimethylpentane.

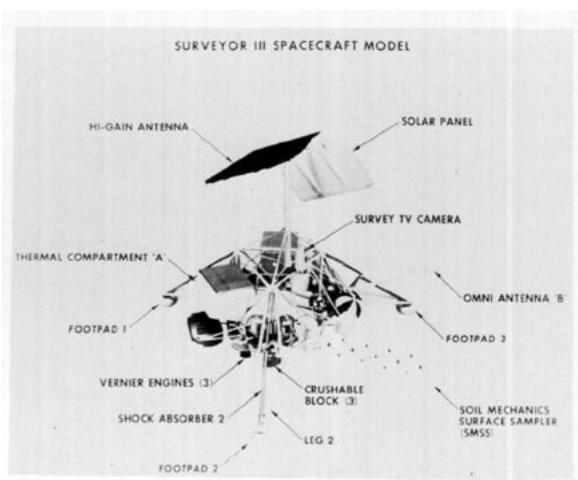

FIGURE 21. Surveyor 3 spacecraft model depicting the most significant areas.

believed that surface contamination would be cleaned up in the space vacuum environment.

Conclusion

Repeated washing of exposed spacecraft surfaces with high-purity anhydrous isopropyl alcohol followed by vacuum baking has been somewhat successful in reducing the overall contamination levels. Incidentally, no conclusive evidence exists of failure of a spacecraft or a particular module because of phthalate contamination. Of course, it is very difficult to have conclusive evidence of

the cause of failure on a nonrecoverable orbiting piece of hardware. Although no failure was involved, the case of the recovered Surveyor hardware was quite enlightening.

With the advent of new and advanced space programs, the size and complexity of payloads, launch vehicles, and test chambers continue to grow. Those working on the development of a manned orbiting laboratory such as Skylab must consider not only these problems but in addition the problems of long-term environmental stabilization and control for the well-being of personnel. As a result of these developments it can be anticipated, and, in fact, preliminary evidence exists, that phthalate as well as other types of contamination problems will emerge on even a larger scale than previously experienced. This does not seem like the type of problem for which there is any straightforward solution; therefore, people connected with all aspects of the space program must be made fully aware of the contamination pitfalls and work to minimize them so that they will no longer pose a threat to the success of a program.

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