Outgassing from internal adhesive joints of vacuum devices

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Abstract：Kinetics of the formation of residual atmosphere in vacuum devices with internal adhesive joints and the application of the mass spectral and chromatographic methods to measure the specific outgassing rate of volatile compounds from the cured adhesives are considered in this paper. The outgassing comparison data for the various types of adhesives are given and the effectiveness of the outgassing of adhesive joints is demonstrated. The possible options to provide vacuum in the various devices are considered. At moderate requirements to the residual pressure (about 10^{-2} Pa), it is enough to degass the adhesive joints during a few hours. It is much more difficult to provide vacuum in devices with internal adhesive joints at the level of about 10^{-4} Pa. This requires the use of the built-in getter and the high temperature degassing. It is expedient to provide deep vacuum ($10^{-5} - 10^{-4}$ Pa) in the rare-used or once-used devices by short (a few minutes) activation the built-in getters before operating the vacuum devices. This allows to remove the main residual gas hydrocarbons component from the vacuum house and provide the necessary level of vacuum for a certain interval of time.

Key words：outgassing；adhesive；vacuum device

0   Introduction

Using adhesives to assemble vacuum and microelectronics devices significantly simplifies the assemble technology and reduces the manufacturing cost of the products. The adhesives allow to joint parts manufactured from different materials easily and firmly. The adhesives have advantages over different solders as they do not require to use flux or carry the assembly in inert medium or under high temperature (300－5 000 ℃).

The main disadvantage of the adhesive joints is gas emission of volatile components from the adhesive surface. Outgassing into the vacuum house of the device forms residual atmosphere that may disturb its function. Usually technical specifications of the adhesive producers include information about temperature mass loss (TML) of the adhesive only，sometimes，and the data about the total amount of extracting volatile components. However for many applications，chemical analysis of the evolved gas is of prime importance. There are some data in Refs. [1-3]，but these results are obtained by different methods and do not allow to define the partial pressure of the volatile components into the vacuum devices with internal adhesive joints during their lifetime. From the practice point of view，researching outgassing from the different adhesives and forming the residual atmosphere in the vacuum devices are of interest to develop optimal adhesive technology and provide the long life-

time for these devices.

The main purpose of this research is to measure outgassing from different cured adhesives and define the residual atmosphere into the vacuum devices with the internal adhesive joints.

1 Kinetics of outgassing from cured adhesive surface

Outgassing from the cured adhesive surface may be characterized by specific rate χ, that is by ratio the emitted mass of gas m from the area to the time of the process t

$$\chi = \frac{m}{St}. \tag{1}$$

If a volatile component i is emitted into volume V during the time t, then the partial pressure of the component P_i is

$$P_i = \frac{\chi_i StRT}{M_i V}, \tag{2}$$

where M_i is the molecular weight of this component, T is temperature, R is the universal gas constant.

The specific outgassing rate of the component i depends on the initial concentration of this component c_{0i} in the cured adhesive and the diffusion coefficient

D_i. The temperature dependences $\chi_i(T)$ and $D_i(T)$ are adequately described by[4]

$$\chi_i(T) = \chi_{0i}\exp\left(-\frac{E_i}{RT}\right),$$

$$D_i(T) = D_{0i}\exp\left(\frac{-E_i}{RT}\right), \tag{3}$$

where E_i is the effective energy of activation, χ_{0i} and D_{0i} are coefficients.

Over time the concentrations of the volatile components in the near-surface zone decrease due to outgassing, therefore the specific outgassing rates of these components decrease. According to the Fick first law for thickness of adhesive layer l, the time dependence of the specific outgassing rate $\chi_i(t)$ at the temperature T may be described by

$$\chi_i(t) = \frac{2c_{0i}M_iD_i}{l}\sum_{n=0}^{\infty}\exp\left[-\frac{D_i(2n+1)^2\pi^2 t}{4l^2}\right]. \tag{4}$$

Under high temperature the concentrations of the volatile components decrease sufficiently fast and the high temperature degassing of the adhesive joints bases on this.

Assume the adhesive layer is degassed during time τ at temperature T_1. After this degassing the time dependence of the specific outgassing rate at some temperature T is given by

$$\chi_i(t,\tau,T,T_1) = \frac{2c_{0i}M_iD_{0i}\exp\left(\frac{-E_i}{RT}\right)}{l}\sum_{n=0}^{\infty}\exp\left[\frac{D_{0i}\exp\left(\frac{-E_i}{RT}\right)(2n+1)^2\pi^2\left(\tau\exp\left(\frac{E_i}{RT}-\frac{E_i}{RT_1}\right)+t\right)}{4l^2}\right]. \tag{5}$$

According to Eq. (5) the high temperature degassing of the adhesive joints during a few hours leads to the same decrease in the specific outgassing rate as being of these joints in normal conditions for several years. For the calculations it is necessary to know $D_i(T)$ and c_{0i}. An example of such calculation is in Ref. [5], however due to small value of the diffusion coefficient of the volatile components in the cured adhesive, one can only use the Eqs. (1)—(3) in most cases. In this case we consider that the specific outgassing rate is constant and equal to the initial one. Then a calculation error will not exceed $20\%-30\%$ for the ten-year period of time.

Degassing is effective but not the only way to provide vacuum in the devices with internal adhesive joints. The emitting volatile components from the

adhesive may be removed from vacuum houses by means of built-in getters. World industry produces a large number of various types of getters, which differ in capacity, design, composition of the getter material and activation temperature. A common feature of all of the getters is their ability to absorb active gasses (hydrogen, oxygen, nitrogen oxide and carbon dioxide, water vapor, etc.), and practically does not absorb non-polar hydrocarbons C_xH_y, although these compounds are typical components of many adhesives[6]. As a result the residual atmospheres of vacuum devices with internal adhesive joints and built-in getters will mainly consist of hydrocarbons released from these joints, which should be taken into account in the calculation of the residual atmosphere parameters.

2 Measurement of outgassing from the cured adhesive

Outgassing from the modern adhesives is very small，so the measuring method must have high sensitivity and selectivity．The most accurate results for outgassing is possible to obtain mass-spectral method．However，despite of the high sensitivity of the mass spectrometer，measuring the outgassing from the cured adhesives at room temperature is difficult．Therefore，to increase the gas flow，surface of the adhesive must be sufficiently large．For instance，in Ref.[5] each researched adhesive was applied on the internal surface of 20 glass tubes and the total surface of the each cured adhesive sample is about 200 cm^2．

To research degassing of the cured adhesive，one can use the kinetic thermodesorbtion mass spectrometry method which is widely used for quantitative studies of gas emission from solids[7]．The measurement procedure includes the quantitative analysis of volatile compounds（H_2O，CO_2，CO，H_2，HCl，Cl_2，H_2S，SO_2，COS，O_2，N_2，NO，NO_2，NH_3，HF，F_2，BF_3，SiF_4，C_xH_y，CH_3OH，C_2H_5OH）emitting from the adhesive in a vacuum at stage heating of the adhesive sample in the temperature range of 80 ℃ to 150 ℃．During each isothermal stage，the flow of products with M/Z from 2 to 220 is measured，wherein the ampoule with the adhesive sample is continuously pumped out．The amount of volatile impurities is determined by integrating the kinetic dependences of the ion current intensity for each impurity using the experimentally determined calibration coeffi-

cient．Then the activation energy of outgassing for each volatile component is determined and the calculated specific outgassing rate corresponds to 25 ℃．The advantage of this method is the high accuracy of determining specific speed of outgassing，however identification of hydrocarbon components is difficult．Usually，the contents of hydrocarbon components are less than the others by several orders of magnitude，which are difficult to measure on this background．Thereby we have to restrict the definition of the average specific outgassing rate for all hydrocarbon components，even though they，as stated above，play a decisive role in the formation of the residual atmosphere in the vacuum devices．

To determine the hydrocarbon components，chromatographic method is used．As practice shows，the sensitivity of the flame ionization detector of the gas chromatograph in relation to hydrocarbons is very high and allows to determine their content up to 10^{-12} mol．In respect of other components，sensitivity of the detector is lower by several orders of magnitude，that is，the chromatographic method allows to track the allocation of only hydrocarbons．Identification of the released hydrocarbon components is carried out based on their keeping time in a chromatographic column．In contrast to the mass spectral method，the preparation of the gas sample is performed by accumulation of volatile components for a sufficiently long time，which greatly increases the sensitivity of this method．The scheme of such accumulation system for measuring volatile hydrocarbon components of the adhesives is given in Fig. 1.

1–Adhesive sample; 2–Pyrex reactor; 3–Electric furnace; 4–Controller; 5–Tap; 6–Gas cylinder; 7–Gas chromatograph; 8–Analog to digital convrter; 9–Computer; 10–Tap; 11–Vacuum gauge
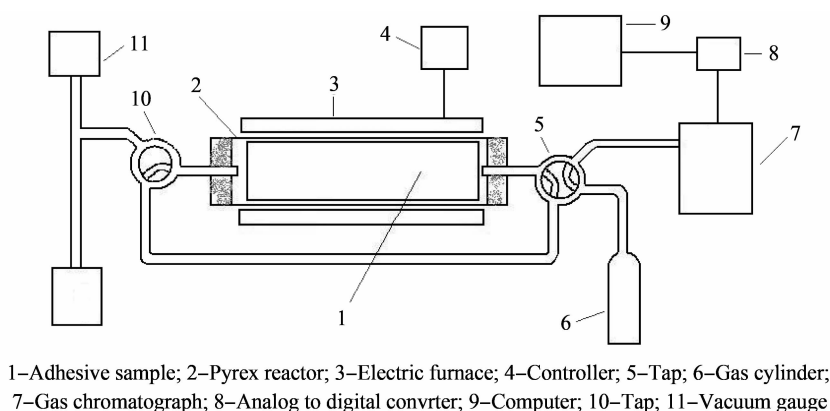
Fig. 1　Accumulation system for preparing gas sample in chromatographic analysis

The adhesive sample 1 (the glass tube with 70 mm-length，7 mm-diameter; the investigated adhesive applies to its inner surface) is placed in a pyrex reactor 2 and inserted in the electric furnace 3. Maintaining the selected temperature of the furnace is carried out by the controller 4. The heating is done in an environment with neutral gas (nitrogen) during 30 — 60 min. During this time the evolved gaseous products accumulate in the reactor. By means of the tap 5 the contents of the reactor 2 is sent to the gas chromatograph 7 with the flame ionization detector by carrier gas of nitrogen (gas cylinder 6). The analog to digital converter 8 records the output signal of this detector and sends the information to the computer 9. This equipment also allows to accumulate emitted volatile components of the adhesive under vacuum. In this case by means of the tap 10，the reactor 2 is evacuated with a vacuum pump. The vacuum level in the reactor 2 is controlled by the vacuum gauge 11. After pumping the reactor 2 with the sample adhesive 1 is disconnected from the vacuum pump by tap 10. Then the adhesive sample is heated to a required temperature for 30—60 min，and then the content of the reactor is directed to the chromatograph for analysis. The advantages of the method are high sensitivity to hydrocarbons，the hardware simplicity and the ability to get results quickly. The disadvantages are the need for calibration of flame ionization detector for hydrocarbons，as well as possible measurement error due to the adsorption of some hydrocarbons on the walls of the reactor and connecting tubes. In general，these methods complement each other and can be used together.

3   Outgassing from different types of adhesives and formation of residual atmosphere in vacuum devices

World industry produces many different types of adhesives: epoxy，cyanoacrylate，inorganic，etc. They differ in chemical composition，thermophysical and strength characteristics，polymerization conditions，etc. The outgassing specific rates of volatile components and their compositions are also different for various types of adhesives.

We measured the kinetics parameters of outgassing process for some Russian and foreign adhesives: epoxy (Epotek H74UNF，H77S，353ND[8]，K-400[9])，ceramic (Resbond 940LE，989F[10]，Cerambond 618N[11])，organo-silicon (OS-52[9])，anaerobic (Anaterm-106[9])，inorganic (VK-21N[9]). The data are given in Table 1 for the room temperature. For another temperature T the specific outgassing rate can be recalculated according to

$$\chi(T) = \chi(T_k)\exp\left[\frac{E}{R}\left(\frac{1}{T_k} - \frac{1}{T}\right)\right]. \qquad (6)$$

All these adhesives are heat-resistant，they are characterized by low shrinkage during drying，low coefficient of thermal linear expansion，high strength and can be used to joint parts of vacuum devices. However，it is seen that their outgassing is very different in both general and on hydrocarbons. Each type of adhesive has its advantages and disadvantages，so the choice of the most suitable adhesive is carried out in each case individually based on the technical requirements of the adhesive joint.

Let us consider，as an example，the possibility of using the epoxy adhesive Epotek H74UNF to joint internal parts of the vacuum devices，which is heat resistant (250 ℃) two-component adhesive with the little TML (0.05%—0.07%) and successfully used in electronic and optical industry. We measured outgassing of the volatile components from this adhesive after additional vacuum degassing at temperature T_1=150 ℃ and 200 ℃ and during τ = 24 h and 144 h. Based on this data we calculated the partial pressure of volatile components in a vacuum device with the Epotek H74UNF joints for S=1 mm^2，V= 1 cm^3 and t=10 years. Table 2 gives results of this calculation for the different regimes of vacuum degassing of this adhesive joints after curing.

These estimates show the outgassing is able to create sufficiently high pressure into the vacuum devices by the end of their service life. If the devices have getters，the residual atmosphere will almost entirely consist of hydrocarbons with the specified pressure in Table 2.

These calculations show that degassing reduces the outgassing very strongly. Also，it completely re-

moves chemically aggressive components，which can interact with the internal parts of the device. If the area S of the adhesive joints is small，the adhesive Epotek H74UNF can be successfully used to assembe various vacuum devices with vacuum at the level of 0.01—0.1 Pa.

Table 1 Outgassing specific rate at $T_k=298$ K and effective energy of activation

Adhesive	Parameter	Volatile component												Total
		H_2O	CO_2	CO	HF	CH_3OH	C_2H_5OH	H_2	HCl	H_2S	SO_2	O_2	C_xH_y	
Epotecny P102	E(kJ/mol)	46.8	60.2	49.1	—	—	—	—	—	—	—	—	—	47.5
	χ (kg/s·m²)	2.2e−11	2.4e−13	5.6e−13	—	—	—	—	—	—	—	—	—	2.3e−11
Epotek H74UNF	E(kJ/mol)	42.5	63.3	63.4	21.3	—	—	31.9	—	—	—	88.7	45.5	68.1
	χ (kg/s·m²)	5.0e−11	1.6e−12	1.9e−12	1.1e−13	—	—	9.4e−13	—	—	—	1.6e−15	1.1e−11	6.6e−11
Epotecny E207	E (kJ/mol)	44.4	112.4	—	59.9	53.1	53.9	42.3	33.4	31.1	—	—	51.0	54.9
	χ (kg/s·m²)	6.0e−11	2.9e−14	—	1.0e−14	2.8e−11	4.1e−13	6.2e−13	3.0e−13	3.2e−14	—	—	8.5e−11	1.7e−10
Epotek 353ND	E (kJ/mol)	33.5	57.0	35.8	35.7	—	22.9	30.1	—	—	—	28.5	32.5	35.4
	χ (kg/s·m²)	1.6e−10	4.0e−12	2.0e−11	3.5e−14	—	9.7e−12	4.4e−13	—	—	—	8.2e−14	1.1e−11	2.0e−10
Epotecny E505	E (kJ/mol)	25.0	59.7	37.3	23.9	—	58.1	31.5	20.6	24.0	—	19.9	28.9	30.1
	χ (kg/s·m²)	1.7e−10	2.0e−12	1.7e−11	8.2e−14	—	1.3e−13	2.9e−13	6.1e−14	8.2e−15	—	2.6e−13	1.8e−11	2.1e−10
Epotek H77S	E (kJ/mol)	68.4	89.8	—	3.4	—	17.2	11.7	—	32.5	—	—	11.6	38.8
	χ (kg/s·m²)	2.2e−12	4.5e−13	—	7.9e−13	—	5.6e−11	1.3e−11	—	1.5e−13	—	—	9.5e−10	1.0e−9
K−400	E (kJ/mol)	31.3	—	—	—	55.7	—	35.2	22.0	—	—	—	31.6	31.9
	χ (kg/s·m²)	1.0e−9	—	—	—	1.1e−11	—	1.3e−12	6.5e−11	—	—	—	5.0e−10	1.6e−9
Resbond 989F	E (kJ/mol)	71.0	123.1	—	—	—	—	—	—	—	—	—	—	72.0
	χ (kg/s·m²)	3.8e−11	5.6e−15	—	—	—	—	—	—	—	—	—	—	3.8e−11
Cerambond 618N	E (kJ/mol)	59.4	44.1	—	—	—	32.9	30.6	—	—	—	—	15.9	32.5
	χ (kg/s·m²)	4.9e−13	1.6e−12	—	—	—	8.5e−12	6.5e−14	—	—	—	—	6.4e−11	7.4e−11
Resbond 940LE	E (kJ/mol)	40.4	72.3	47.9	38.8	—	—	29.7	56.0	68.1	50.3	34.1	54.2	41.0
	χ (kg/s·m²)	1.9e−10	2.6e−13	4.9e−13	1.9e−14	—	—	4.6e−13	4.5e−15	3.0e−16	4.7e−15	2.3e−13	1.1e−13	1.9e−10
VK-21N	E (kJ/mol)	35.8	36.1	53.8	56.1	—	—	61.8	61.9	51.3	—	58.5	39.3	35.9
	χ (kg/s·m²)	6.6e−10	1.9e−12	6e−13	1.3e−14	—	—	2.3e−14	2.3e−14	1.2e−15	—	6.3e−14	1.8e−12	6.6e−10
OS-52	E (kJ/mol)	49.1	46.6	39.4	—	45.2	33.6	24.0	—	—	—	—	40.4	44.4
	χ (kg/s·m²)	1.1e−11	2.9e−13	1.9e−12	—	8.9e−14	1.1e−13	8.6e−13	—	—	—	—	2.0e−12	1.3e−11
Anaterm-106	E (kJ/mol)	64.9	70.1	—	47.3	33.7	83.0	36.6	—	—	70.0	—	31.7	42.5
	χ (kg/s·m²)	3.7e−12	2.6e−12	—	3.1e−14	3.3e−11	3.0e−14	2.4e−12	—	—	1.7e−13	—	1.4e−10	1.8e−10

Table 2 Partial pressure of volatile components into vacuum device with internal adhesive joints in 10 years after manufacturing

Regime of degassing	Partial pressure (Pa)							Total pressure (Pa)
	H_2O	CO_2	CO	C_xH_y	H_2	O_2	HF	
$\tau=0$	2 174	28	5.4	315	378	0.04	4.4	2 905
$\tau=24$ h；$T=150$ ℃	0.12	10^{-4}	0.004	0.02	0.03	0	0	0.14
$\tau=144$ h；$T=150$ ℃	0.03	4×10^{-5}	0	0.05	0	0	0	0.08
$\tau=144$ h；$T=200$ ℃	0.008	2×10^{-5}	0	0.009	8×10^{-4}	0	0	0.017

It is more difficult to provide vacuum in devices with internal adhesive joints at the level of about 10^{-4} Pa. Table 2 shows that only long-term annealing at high temperature and using the built-in getter allow to provide vacuum of not worse than 0.01 Pa for 10 years after manufacturing. The more deep vacuum can be obtained in the devices with a relatively large internal volume (about 100 cm³), or with significant reduction in the exposed surface of the adhesive.

For rare-used or once-used devices with internal adhesive joints，deep vacuum can be achieved by briefly switching the getters directly before using the devices. This possibility is connected with the properties of the getters：their activity in relation to hydrocarbons increases significantly with increasing temperature. Under heating the most of the getter materials up to 450—500 ℃，the pyrolysis of hydrocarbon molecules C_xH_y occurs on their surface. The pyrolysis products are adsorbed by active surface centers of the getter forming solid stable chemical compounds. In other words，the short-term activation of the getter before the device operating allows to ensure the deep vacuum for a period of from several hours to several days. This time (after the activation of the getter) can be estimated by

$$t = \frac{p_D V M_{C_xH_y}}{SRT\chi_{C_xH_y}}, \qquad (7)$$

where P_D is the maximum allowable pressure inside the device.

For example，let the device has the internal volume $V=1$ cm^3，the area of internal adhesive joints $S=1$ mm^2 and the maximum gas pressure must not exceed $P_D=10^{-4}$ Pa. If $\chi_{C_xH_y}=10-11$ kg/s • m^2 and $T=298$ K，then the uptime of the device after activation of the getter is about 3 h.

This example shows that after the activation of the getter the vacuum device is able to operate for a long time，even if degassing of its adhesive joints is not performed and the outgassing from the internal adhesive joints is sufficiently large. In this case the periodic regime of the getter operation allows，on the one hand，to provide the necessary level of vacuum in the device，and on the other hand，to simplify the manufacturing technology by eliminating long outgassing of the adhesive joints. However，the periodic activation of the getter does not allow to provide the long-term operation of the vacuum device due to the limit on the number of the activation of the getter (usually less than 100).

4　Conclusion

This investigation shows that providing the necessary vacuum in the devices with the internal adhesive joints is a complex task. The successful solution of this task requires not only the optimal choice of the adhesive but also the rational choice of the geometry of the adhesive connection，the regime of degassing and the getter.

The application of the adhesives to joint the parts of vacuum devices is optimal at moderate requirements for the maximum allowable pressure inside the device is about 10^{-2} Pa. In these cases it is sufficient to degass the adhesive joints during a few hours.

It is much more difficult to provide vacuum in devices with internal adhesive joints at the level of about 10^{-4} Pa. This requires the use of the built-in getter and the high temperature degassing.

It is expedient to provide deep vacuum ($10^{-5}-10^{-4}$ Pa) in the rare-used or once-used devices by short activation (a few minutes) of the built-in getters before applying the vacuum devices. This allows us to remove the main residual gas hydrocarbons component from the vacuum house and provide the necessary level of vacuum for a certain interval of time. This approach allows elimination of long degassing of the internal adhesive joints for the rare-used or once-used devices.

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真空装置内部粘合接头的脱气

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摘　要：　本文讨论了有内部粘接剂的真空装置内的残余气氛形成的动力学，以及质谱和色谱方法在测定固化胶粘剂中挥发性化合物的比气率的应用。本文给出了各种类型的胶粘剂的脱气比较数据，并证明了胶粘剂接头脱气的有效性。同时也考虑了在各种设备中提供真空的可能选项。对于残余压力（约 10^{-2} Pa）的适当要求下，在几个小时内就足以对粘合剂接头进行脱气。在大约 10^{-4} Pa 压力下，在有内部粘合接头的装置中提供真空要困难得多，这需要使用内置的吸气剂和高温去气。在使用真空装置之前短时间（几分钟）激活内置吸气剂，在基本不通或曾经使用过的设备上提供深真空（$10^{-5}-10^{-4}$ Pa）是有利的。这可以去除主要的残余碳氢化合物气体成分，并在一定的时间间隔内提供必要的真空水平。

关键词：　脱气；粘接剂；真空装置