# Anaerobic Adhesive Jetting For Microelectronics Packaging Applications

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## ABSTRACT

Anaerobic fluid has been used as an industrial adhesive to seal or bond metal components for both large and small-scale applications. Its use has recently extended to microelectronics packaging. Part handling at micro-scale dimensions and the need for high production throughput bring challenges to dispensing anaerobic fluid for this novel application. Most high-precision dispensers have fluid paths that are constructed of metal components to ensure product robustness and enable dimensional precision of micro-scale parts. This is incompatible with anaerobic adhesives which cure in the absence of oxygen and utilize metal ions as the catalyst. Furthermore, curing accelerates when confined to a small area. A non-contact jetting solution has been developed and applied in a production environment to dispense anaerobic adhesives with precise volume control, at high speed, and with continuous operation. Dispensing can be optimized to include a range of hardware dimensions, component surfaces, fluid handling methods, and process controls.

## INTRODUCTION

Anaerobic adhesives are mixtures of acrylic esters that remain liquid when exposed to air, but harden when confined between metal surfaces [1]. They cure in the absence of oxygen and utilize metal ions as the catalyst. These adhesives are broadly used in industry, for example, to lock threaded fasteners, seal threaded pipe connections, and to bond cylindrical fitting parts. The first formulation was made by General Electric and then the process was optimized by Vernon Krieble. For practical storage and shipping, he used a reaction initiator [2][3] and packaged the adhesive in half-filled oxygen-permeable polyethylene bottles. He licensed this solution and in 1954 founded a company that later became Loctite Corporation. Since then, hundreds of patents have been filed for formula improvement and technical innovations. Nowadays, its applications cover many industries all over the world and thousands of tons of these products are used every year.

Polymerization, needed for most adhesives to cure, is a process of reacting monomer molecules together in a chemical reaction to form polymer chains. Anaerobic adhesives cure by radical polymerization. The cure mechanism [1][2][3] is shown in figure 1, using Loctite 661 and 638 anaerobic adhesives on a steel substrate as an example. At first, Cumene hydroperoxide ROOH (initiator 5% by weight) initiates the cure by triggering an oxidation reduction reaction with a transition metal, e.g. iron, on the substrate surface that releases free radical RO•. These free radicals, namely unpaired electrons, are unstable and initiate polymerization of the urethane methacrylate resin M in 661 and 638 to produce free radical P•. The methacrylate free radical P• combines with another resin molecule M, and a polymer chain grows. In the absence of oxygen, this polymer chain propagates until termination occurs. With oxygen, polymer radicals are more reactive and yield peroxy free radicals which then react with resin M to propagate another polymer chain. In a confined area, oxygen is consumed quickly, which allows the adhesive-curing chain reaction to propagate.

(1) $Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO\cdot + OH^{-}$

$R = C_6H_5C(CH_3)_2$

(2) $RO\cdot + M = P\cdot$

(3) $P\cdot + M = \sim\sim P\cdot$

(4) $\sim\sim P\cdot + \cdot P\sim\sim = \sim\sim PP\sim\sim$ Or (5) $\sim\sim P\cdot + O_2 = \sim\sim P-O-O\cdot$

$\sim\sim P-O-O\cdot + M = \sim\sim P-O-O-M\cdot$

***Figure 1: Cure mechanism of anaerobic adhesives Loctite 661 and 638 on a steel substrate. The process involves: (1) radical formation, (2) reaction chain initiation, (3) chain growth, (4) polymerization without oxygen, (5) with oxygen.***

Due to their property of curing quickly in a confined area, it is difficult to handle anaerobic adhesives in dimensions as small as one millimeter, so these adhesives have mostly been used for industrial purposes. In recent years, however, anaerobic adhesive use has expanded to microelectronics packaging. For example, they are being used to bond small components in microelectronic devices used in the automotive and portable electronics industries. These applications require high precision and throughput, necessitating involvement from the full supply chain.

Recently, some of our customers in the portable electronics industry wanted to dispense two Loctite anaerobic adhesives for their MEMS devices. The dispense specifications included volumetric repeatability of 25 nanoliters at 3 sigma and throughput of 1 unit per second. Like most dispensing equipment, the fluid path of our high-precision dispensers is constructed of metal to ensure valve robustness and to enable dimensional precision of micro-scale component parts. As mentioned, metal is incompatible with anaerobic adhesives which cure in the absence of oxygen and utilize metal ions as the catalyst. Furthermore, the narrow fluid paths designed for small volume jetting accelerate the curing process of these adhesives.

A non-contact jetting solution to dispense anaerobic adhesives with precise volume control, at high speed, and in a continuous operation has been developed and applied in a production environment. Dispensing is optimized to include a range of hardware dimensions, component surfaces, fluid handling methods, and process controls. This paper will present the development of the process, design of experiment (DOE), and mechanism analysis of the results.

# DISPENSING SOLUTION

To fulfill the demands of this application for precision dispensing of small amounts of fluid and high volume production, Nordson ASYMTEK's DJ-9500 jetting valve was chosen for feasibility testing because of its high-speed capabilities and non-contact jetting. Curing mechanisms were carefully taken into account as part of the DOE parameters. Then, the contribution of each factor was quantified and classified as primary, secondary, etc. This study helped to develop an approach that could fulfill the application's specifications.

Factors included in the experiment were (1) component dimensions, i.e. orifice sizes or confined areas along the fluid path (figure 2), (2) component materials, (3) the maintenance and cleaning processes needed for the dispenser, and (4) fluid temperature, since radical polymerization is temperature sensitive. Based on the dispense volumes that were specified, and for volumetric accuracy, a nozzle orifice of 0.1 - 0.125mm was needed to jet the adhesives. This small size provides a flow rate resolution within a few nanoliters. This small nozzle orifice, as well as the needle that provides the momentum for the fluid to move out and break off from the nozzle, had to be made of rigid and strong materials, such as metal and metal alloys. Using metal created a conflict because metal promotes curing of the anaerobic adhesives, so plastic components and surface coatings were considered as alternative solutions to dispense these adhesives.

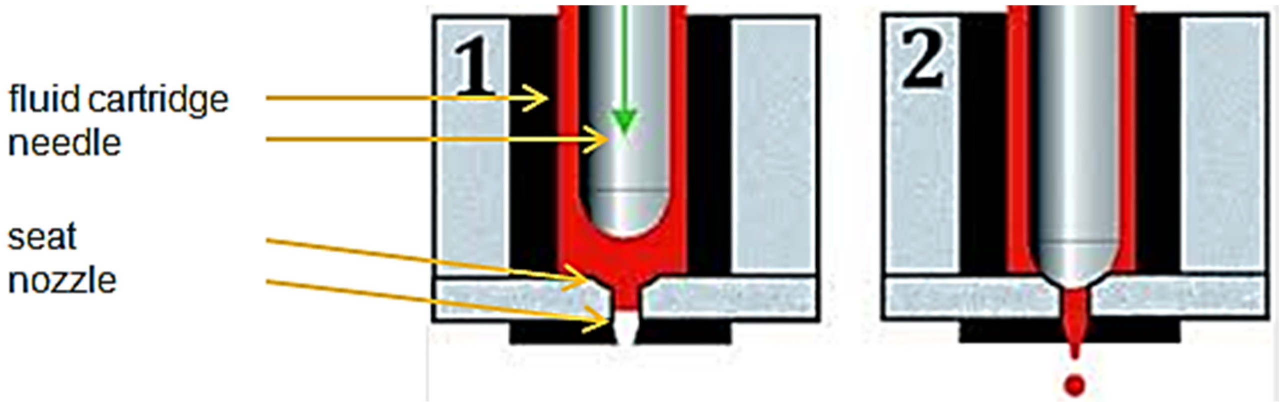


***Figure 2: Confined areas along fluid path (red) in DJ-9500 valve when (1) valve opens, (2) valve closes.***

While anaerobic adhesives cure in a confined small area between most metal surfaces, active metals promote curing the quickest. For example, copper, iron, and steel are very active; stainless steel, carbide, and aluminum are less active; and other special alloys are inactive metals. For our application, the least active metal alloys were recommended in the construction of three of the DJ-9500 jet valve's components that are used along the fluid path: the fluid cartridge, needle, and nozzle. The only component made of plastic was the seat. It has an orifice size larger than 0.2mm so it can be made of plastic with good surface finish. The seat also contacts the metal needle during valve off time, with an interface filled with adhesives that would have quickly cured if both surfaces were metal. A special polymer was selected for the seat material.

Anaerobic adhesive still cures between the less active metal surfaces, however, at a slower speed. To reduce the risk of curing, more rigorous maintenance was applied during dispensing, for valve idle times, and the cleaning process. Frequent purges during idle times are recommended to reduce or eliminate fluid stagnation along the metal surfaces. The purge frequency necessary to maintain clog-free dispensing was tested for different metal surfaces and orifice dimensions. The automated purge amount was set at 5mg based on the retained volume along the fluid path.

Two different valve orifice dimensions were tested, one to produce a medium flow rate of 0.2mg/shot and the other for a low flow rate of 0.02 - 0.06 mg/shot. The anaerobic adhesive definitely cured more quickly when flowing through the small orifices, making the MEMS application more challenging. Plastic material was not used for components with an orifice size smaller than 0.2mm, such as the nozzles in size 0.1-0.125mm. Due to burrs in plastic, surface finishing of the small plastic nozzle produces poor dimensional tolerance. Since the application was to test the feasibility of jetting small, high-precision dots, plastic nozzles were not considered.

Experiment data shows the different curing speeds of the two anaerobic adhesives, Loctite 661 and Loctite 638, within the DJ-9500 valve during jetting. Tests include different seat and nozzle sizes; different component surfaces, e.g. stainless steel, carbide, other alloys and plastic; and different maintenance frequency, e.g. purge every 2, 4, 15, or 60 minutes. For each condition, the appearance of plugging (no fluid out) or soft clogging (significant flow rate drop) defines the maximum continuous operation time. After that, the valve needs to be completely cleaned in solvent to avoid having the adhesive fully curing within the valve.

The challenges to jet these two adhesives are different. The technical data sheets (TDSs) show that Loctite 661 has a viscosity of 400cP and Loctite 638 has a viscosity of 2500cP. The lower viscosity makes the 661 easier to jet; however, the TDSs also indicate that it cures faster than the 638 on the same metal surface. The Loctite 638 application requires a finer volume resolution than the 661, thus the adhesive needs to go through a more narrowly confined fluid path. For this lab study, we also tested the 661 jetting at a low flow rate for comparison.

# RESULTS

Experiments were designed and conducted in the lab (table 1). Tests included changes in (1) the dimensions of the DJ-9500 components that resulted in medium to low flow rate range, (2) valve component materials made out of stainless steel, carbide, special alloys, or polymers, and (3) dispense maintenance frequency. More than 30 experiment runs were conducted.

| Adhesive | Flow rate (mg/shot) | Special surface, Yes/No | Fluid temperature (ºC) | Max purge interval (minute) | Clog after 1 Hr idle, Yes/No |
|---|---|---|---|---|---|
| Loctite 661 | 0.22 | N | 28 | 15 | N |
| 661 | 0.11 | N | 28 | 15 | Y |
| 661 | 0.11 | Y | 28 | 15 | N |
| 661 | 0.04-0.06 | N | 28 | 4 | Y |
| 661 | 0.04-0.06 | Y | 28 | 15 | N |
| Loctite 638 | 0.02-0.06 | N | 35 | 4 | Y |
| 638 | 0.02-0.06 | Y | 35 | 15 | N |
| 638 | 0.02-0.06 | Y | 55 | N/A, clogs immediately | N/A |

***Table 1: Design of experiments and results. Control parameters include (1) two adhesives, (2) narrow fluid path quantified by resulting flow rate, (3) component surface materials as special or standard, and (4) fluid temperature. To pass for production, specifications include: (1) no clogging during 12-24 hours of continuous operation with purge frequency every 15 minutes, (2) no clogging after 1 hour of idle time.***

### (1) Regular maintenance during and post dispense

This seemed to be one of the most critical factors in keeping curing under control. Lab tests confirmed that the adhesives cured along the metal surfaces they were contained in if the valve idled long enough. With the same metal surfaces and spaces in between, a more frequent maintenance regimen during dispensing idle times extends the maximum hours of continuous operation from less than 1 hour to 20 hours. For example, a soft gel doesn't appear until around 20 hours if the valve purge routine is set to dispense a certain amount every 15 minutes, and longer if it is set to dispense every 2-4 minutes.

In order to meet production environment specifications, the following requirements were applied for the tests: (1) no clogging during 12-24 hours of continuous operation at a purge frequency of once every 15 minutes, and (2) no clogging after an occasional 1 hour idle. These specifications were based on operation convenience as observed at the customer's production site.

### (2) Orifice dimensions

The orifice dimension along the fluid path is the second critical factor affecting anaerobic fluid curing. The narrower the orifice, the quicker the adhesive gels. The data shows that good non-curing results during a continuous dispensing operation can be obtained for Loctite 661 at a flow rate of 0.2mg/shot, using a 1.5mm inner diameter seat and a 0.25mm nozzle made with standard metal components. In contrast, using the same component material, purge frequency, and nozzle, but with a smaller seat inner diameter of 0.38mm (0.1mg/shot), the 661 started to cure within the seat, but downstream the nozzle was clean. After an idle period of one hour, the flow rate dropped by 20% and the seat was partially plugged. With the fluid path confined within a smaller nozzle of 0.1mm and the flow rate at 0.04-0.06mg/shot, curing was initiated within the nozzle, while upstream the 0.38mm seat was clean. In this condition the nozzle became completely plugged.

Loctite 638 was tested only at low flow rates of 0.02-0.06mg/shot upon customer request; hence, components with small orifices were used, e.g. a 0.38mm seat and a 0.1 - 0.125mm nozzle. Experiment results (table 1) show that at a low flow rate, the standard component material was unable to maintain non-curing continuous operation. With these small orifices that result in a low flow rate, the jetting process needs either more frequent purges, such as once every 2-4 minutes, or special component materials.

**(3) Component materials/surfaces**

The most interesting factor involving anaerobic adhesive curing is the different materials that compose the walls of the narrow fluid path. Stiff and rigid metals are typically chosen to construct most of the fluid path due to the requirement of component strength and dispensing precision. The least active metals are the recommended materials to make the nozzle, needle, and fluid cartridge for this application. Special plastic is recommended for the seat which the metal needle makes contact with during the jetting process and valve idle times. The test shows that this design provides the optimal solution for the surfaces in which the anaerobic adhesive is contained. Both Loctite 661 and Loctite 638 can be jetted through small spaces at fine volumetric resolution and with continuous operation, e.g. to jet 638 at 25 nanoliters per shot and maintain 12-24 hour continuous operation with a purge routine every 15 minutes.

**(4) Fluid temperature**

High temperature significantly promotes curing. A nozzle temperature of 55$^{o}$C was tested to help improve jetting Loctite 638, but flow rate fluctuations and frequent nozzle plugging were observed. In general, heating is not recommended for dispensing anaerobic adhesives. For this application, a nozzle temperature of 35$^{o}$C is used to reduce fluid viscosity for jetting and to match the maximum possible room temperature in production environments. A nozzle temperature of 28$^{o}$C is used for Loctite 661. Constant fluid temperature is recommended to maintain a stable flow rate, hence repeatable dispensed volumes.

## CONCLUSIONS AND DISCUSSION

When dispensing anaerobic adhesives in large to medium volumes of fluid, standard metals can be used to manufacture the DJ-9500 valve components. Good results will be obtained by following a careful maintenance regimen of purging the dispense valve every 15 minutes and cleaning the system within 24-48 hours. For dispensing anaerobic adhesives in small volumes for microelectronic applications and to minimize curing during the dispensing process, valve components should be constructed using inactive alloys and plastics. The valves should be purged every 15 minutes and cleaned within 12-24 hours.

In summary, we have presented a solution for the challenging application of jetting anaerobic adhesives with volumetric precision and high throughput. Our solution fulfills the customer’s specifications, at a reasonable cost, and requires minimum maintenance. This solution is now running on 25 machines in a production line with 24-hour continuous operation.

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