

Impact of separator design on the performance of gelled-electrolyte valve-regulated lead/acid batteries

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Abstract

The special requirements of separators used in the manufacture of gelled valve-regulated lead/acid (VRLA) batteries start at the cell-processing steps, where the separator must assist, through its characteristics, the formation of an optimal gel structure. In a gelled VRLA cell, conditions exist that pose additional demands on the separators. In this type of cell, the separator is not a by-stander, but an integral link in the chain of events that comprise the establishment of an efficient oxygen-recombination cycle. In the work reported here, the need for separator materials of very high porosity will be demonstrated, as well as the need for optimal pore size distributions. An examination is also made of the effect of the surface characteristics of the separator on the formation of gel micro-channels and, in turn, the efficiency of the oxygen cycle. © 1997 Published by Elsevier Science S.A.

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1. Introduction

Valve-regulated lead/acid (VRLA) batteries of the gelled-electrolyte design have been available for some time. In the beginning, this technique was transplanted from the nickel-cadmium to the lead/acid battery without much thought of the peculiar needs of the latter. Materials available at the time were used in those early designs (instead of developing new, purpose-designed materials) and since inertia is always the hardest thing to overcome, the situation has evolved only slowly since then.

Today, however, the requirements are changing. Across the entire technological spectrum, specificity is the order of the day. Devices are designed for very precise applications, and top performances are expected of every item produced. The gelled VRLA battery is no exception. Given its advantages as a valve-regulated, low-gassing battery, supplemented by proven superior performance in deep-cycle applications, this type of lead/acid technology has a very bright future indeed.

The present and future development of gelled VRLA batteries will be along lines of specific designs for specific

uses. This paper concentrates on a key design item, namely, the separator. The latter has a role that goes beyond that which is often mentioned in literature [1–3] for flooded lead/acid battery systems. In particular, the separator in gelled batteries has to be seen as an integral part of the all-important oxygen transport mechanism, upon which the good functioning of the VRLA cell rests.

The gelled electrolyte and the separator must be treated as two inter-related components of the single process of oxygen transport. In order to achieve the required result, each component must be optimized. The following will give a clearer definition of this inter-relation and how it affects the performance of gelled VRLA cells. In other words, it is examined how these two components can be selected to achieve the best performance for each specific application.

2. Influence of separator characteristics on the manufacturing process of gelled VRLA cells

The manufacture of any gelled VRLA cell has to follow special conditions [4]. Care must be taken during each manufacturing step to assure the highest possible degree of compliance to very demanding specifications. This need to

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meet exacting standards apply equally to the separators that are used in the assembly of gelled VRLA cells. Thus, the separators must fulfill certain physical and electrochemical functions during their service life. This section deals with the required physical functions.

The distinguishing manufacturing step that sets gelled VRLA cell assembly apart from other lead/acid battery technologies, is the electrolyte gel-formation process. This process consists of creating a three-dimensional silica gel structure in which the electrolyte is immobilized. In practice, the gel is obtained by introducing into the cell electrolyte very fine particles of silica (normally, fumed silica with an average aggregate size of only a few nanometers in diameter). These particles react with the sulfate ions of the electrolyte and solidify in the desired three-dimensional gel matrix [5]. The silica particles can be introduced into the cell either dissolved in sulfuric acid solution or simply dissolved in water. Thus, the filling process of gelled VRLA cells is a very critical one, and one in which the separator plays a significant part.

2.1. Filling techniques for gelled VRLA cells and separator characteristics and design

At this point, a distinction must be made between two types of filling methods for gelled VRLA cells (Fig. 1). In one case, the cell element is in a dry state, whereas in the other process, the element is already moist. In both cases, it is very important that the separator exhibits good wetting characteristics, but it could be argued that high wettability is particularly important when filling cells with dry elements. Here, instant penetration by the silica-containing electrolyte is very important. Wetting times of fractions of a minute are required. The price to be paid for allowing cells to be poorly filled is high; it is expressed in terms of increased electrical resistance and poor cell performance.

Another factor to be considered is the influence of separator rib profile in the filling process. When filling with silica-containing electrolyte mixtures of varying viscosities, it is important that good contact has been made everywhere inside the cell between the incoming electrolyte and all other cell components. Vertical, or near

vertical, separator profiles and smooth surfaces are deemed to be advantageous. In the case of filling moist elements, this criteria is not so strict, and a greater degree of freedom exists as far as separator profile is concerned.

2.2. Function of the separator in gel setting

What then is the role of the separator during gel formation? As far as is currently known, gel formation is not influenced by the type of separator used, or by its design. This process depends rather on the relative amounts of the key ingredients, such as very fine silica particles and the sulfate in the electrolyte. It is in fact the presence of sulfate ions that creates the liquid/solid transition state known as a gel.

A topic for future investigation could be the influence on gel setting of the different silica-bearing separator systems, particularly those separators that either have no silica or have a large amount of it available on their surfaces.

3. The separator as a key component for the proper functioning of an efficient gelled VRLA cell

In this section, consideration is given to the most important role of the separator and its impact on the electrochemical performance of the gelled VRLA cell.

3.1. Theory of gel micro-channel structure for oxygen transport

Although the chemistry of silica gel formation is generally well understood, the mechanism by which gel behaves in the context of a lead/acid cell is not so clearly defined. Nevertheless, some general observations can be made and a theory can be advanced as to how silica gel operates inside the VRLA cell.

Initially when the silica gel is formed, there is total water saturation. The gel structure is completely filled with the electrolyte, which is also present in the active material and in the gel/electrode surface interfaces. Thus, in the first few cycles, the gelled VRLA cell functions much as a flooded lead/acid cell and water loss occurs, particularly at the end of the charging periods.

At this stage, it must be recognized that, depending on what process path is chosen to achieve gell formation, there will be different gel consistencies. For example, some gellification techniques result in a gel whose structure is relatively weak and only very low shear forces are required to break it. The situation is illustrated in Fig. 2, where an approximation is made of the amount of cycling required to achieve recombination with the different types of gelled electrolytes. In this scenario, the water that is lost during the initial charging cycles, permits a very slight

DRY ELEMENT FILLING METHOD:

- Separator WETTING must be thorough and quick.
- Separator RIBS should preferentially be vertical or near vertical.
- Separator SURFACE should be smooth.

MOIST ELEMENT FILLING:

- Separator WETTABILITY is important.
- Separator RIB design can be of any orientation.

IMPACT OF SEPARATOR TYPE AND DESIGN ON GEL SETTING: None known.

Fig. 1. Separator characteristics required for good filling of the gelled electrolyte filling.

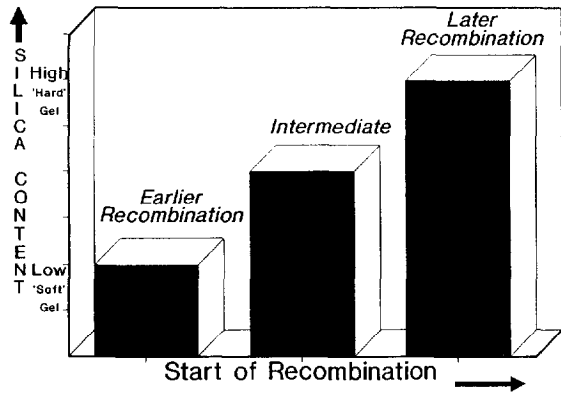


Fig. 2. Relative gel consistency vs. approximate start of recombination.

dry-out of the gel structure, and only then does the incoming oxygen gas have a chance to create the micro-channels along which it can move.

Since oxygen is liberated at the positive plate as a gas, it naturally has a tendency to follow the path of least resistance and travel preferentially upwards. The path of the active-material/gel interface is blocked, however, by the presence of an electrolyte film. Once sufficient pressure is built up, oxygen gas has to make its way through the gel itself. The possible paths that the gas can follow is shown in Fig. 3. (Note, this process of gel cracking is totally random, but it is logical to assume that the areas where the gel structure is the weakest will contain the highest density of micro-channels.) It is also common sense to assume that separator rib design can have an influence in 'guiding' the formation and general direction of the micro-channels that are created, although the separator itself does not participate in the micro-channel generating process.

At this early stage of electrolyte saturation, it is reasonable to assume that since the separator is totally saturated with electrolyte, it will not allow any passage of gas. All gas transport will be around the element edges. As water is lost from the cell, however, the situation changes as will be demonstrated below.

The situation is slightly different for VRLA batteries in which the electrolyte is immobilized in an absorptive glass

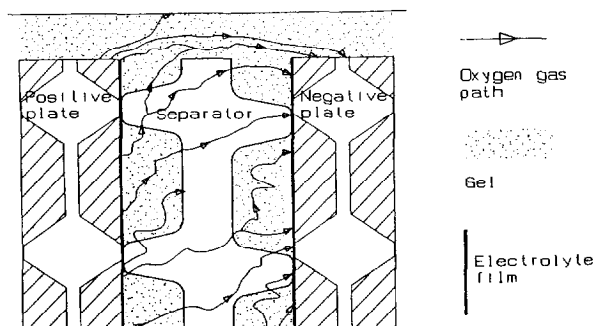


Fig. 3. Possible paths of oxygen gas through the gel during the first cycles.

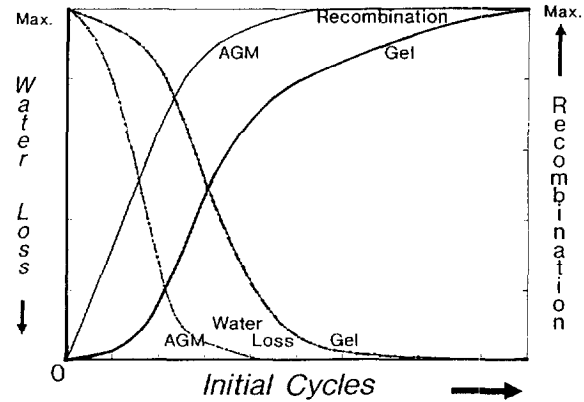


Fig. 4. Initial water loss and start of recombination in AGM and gelled-electrolyte VRLA cells.

micro-fibre (AGM) separator. In this case, sufficient free space exists between the active-material/separator interface to allow for the upward movement of oxygen gas. Oxygen reduction at the negative plate, with the resulting water recovery, is then relatively easier to achieve and it occurs earlier in the cycle life of the VRLA cell, as illustrated in Fig. 4.

3.2. The significance of high porosity

Before launching into a full-scale discussion of the relative impact of separator porosity and pore size on cell performance, it is well worthwhile to pause and analyse these very important separator characteristics.

Generally, separator porosity refers to all the void spaces that exist within the structure of the separator. In the case of the silica-containing separators, there are two sources of void volumes:

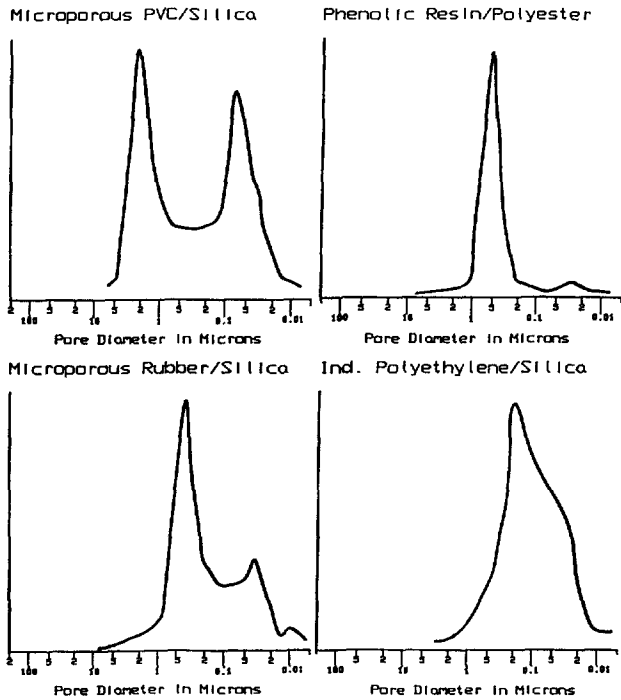
1. extraction/curing void volume: this is created by the extraction of a liquid that was introduced during the extrusion step of the separator manufacture, or by the curing step of resins or rubber/latex compounds, and
2. silica agglomerate void volume: this is the empty space that exists within each silica agglomerate; it is the space between the constituent silica aggregates.

Comparison of the different silica-bearing separator systems discloses different ratios of these two types of void volumes. This is illustrated in Fig. 5 for four types of separator that contain silica.

Pore size, on the other hand, is a the measure of the average diameter of voids created either during the extraction/curing process and also a measure of the average empty spaces within the silica agglomerates.

In the case of AGM separators, the void volume and average pore size is simply the amount and size of empty volumes between the fibres.

In the context of gelled VRLA cells, it is generally accepted that separators must be of very high porosity. The first reason for this requirement is that the separator has to



Note: Values obtained by Mercury Intrusion Porosimeter

Fig. 5. Pore-size profiles of different microporous separator systems.

be seen as an electrolyte reservoir. The separator must retain as much of the electrolyte as possible in its structure. A separator of low porosity will help to reduce the volumetric density of the cell and, thus, lower its overall efficiency.

In order to measure how oxygen gas can be transported across a separator material, a simple experiment was designed to measure the degree of permeability of different microporous separators [6]. A schematic view of the experimental apparatus is shown in Fig. 6, and some typical results are given in Table 1. It should be noted that the gas pressure range selected for this permeability study was 0 to 140 mbar. This corresponds to the medium pressure range that exists inside VRLA cells. The study of separator permeability confirms that an acid-saturation level in the separator of at least 95% is needed for gas movement to occur across the medium-to-high porosity separators. By

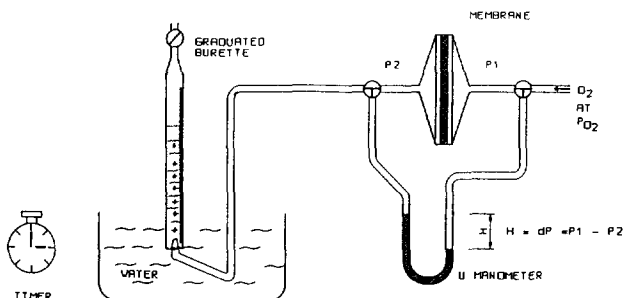


Fig. 6. Apparatus for measurement of the oxygen permeability of different separators.

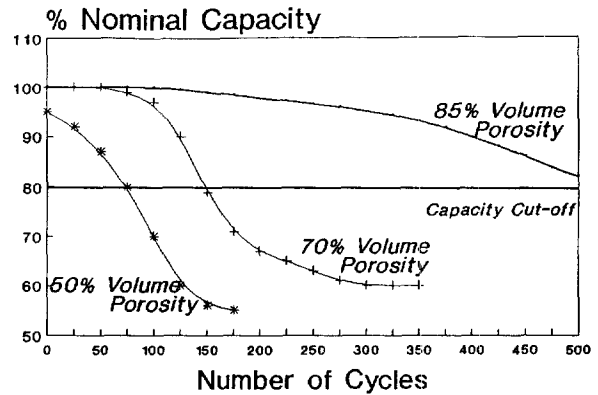


Fig. 7. Impact of the separator porosity on the electrical performance of 130 Ah gelled VRLA cells with tubular positive-plates.

contrast, low-porosity separators provided a barrier to oxygen transport until an electrolyte saturation of 75% was reached. In effect, this means that during the useful life of gelled VRLA cells, these low-porosity separators are always acting as gas barriers and force oxygen gas transport around the element edges.

Laboratory tests conducted on gelled VRLA cells of 130 Ah capacity show that, for this particular cell size, the impact of separator porosity on the number of life cycles is quite dramatic, see Fig. 7. For example, the low-porosity separator (50%) delivered only 75 cycles as opposed to ~ 150 cycles for the medium-porosity separator (70%). The high porosity separator (85%) delivered 500 cycles. In this particular test, no consideration was given to pore size and this was quite different for the three separator types.

3.3. The importance of optimal pore-size distribution

Experimental data support the idea that, for given gel structures, there are optimal separator pore sizes. The data in Fig. 8 show that for this particular type of gel, separators with mean pore sizes of 1 to 10 μm have superior performances.

The exact impact of separator pore size on gelled

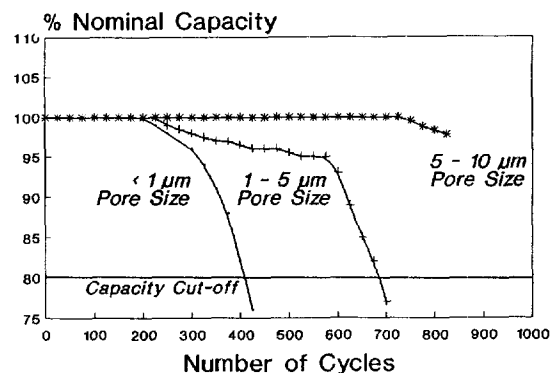


Fig. 8. Impact of the separator pore size on the electrical performance of gelled VRLA cells.

Table 1

Oxygen gas permeability of various wet separator materials. The nominal electrolyte saturation level is $85 \pm 5\%$. All permeability values are in $l/(\text{min cm}^2)$

Oxygen pressure (mbar)	Very high porosity PVC	High porosity PVC	Standard porosity PVC	Phenolic resin/polyester	Polyethylene SLI grade	Polyethylene industrial grade
20	0.0008	0.0012	0.0013	0.0013	no flow	no flow
40	0.0019	0.0020	0.0020	0.0017	no flow	no flow
60	0.0040	0.0030	0.0025	0.0025	no flow	no flow
80	0.0076	0.0046	0.0033	0.0034	no flow	no flow
100	0.0130	0.0072	0.0042	0.0040	no flow	no flow
120	0.0280	0.0100	0.0053	0.0050	no flow	no flow
140	0.0400	0.0140	0.0074	0.0070	no flow	no flow

VRLA cell performance is still being investigated and will be the topic of a future study. Nevertheless, when relating the impact of separator pore size to optimal cell performance, careful consideration must be given to the type of gel that

exists within the cell. A 'hard' (high silica content) gel calls for a pore size of the order of μm , whereas a 'soft' (low silica content) gel requires a more closed separator structure for its optimal functioning. Naturally, the require-

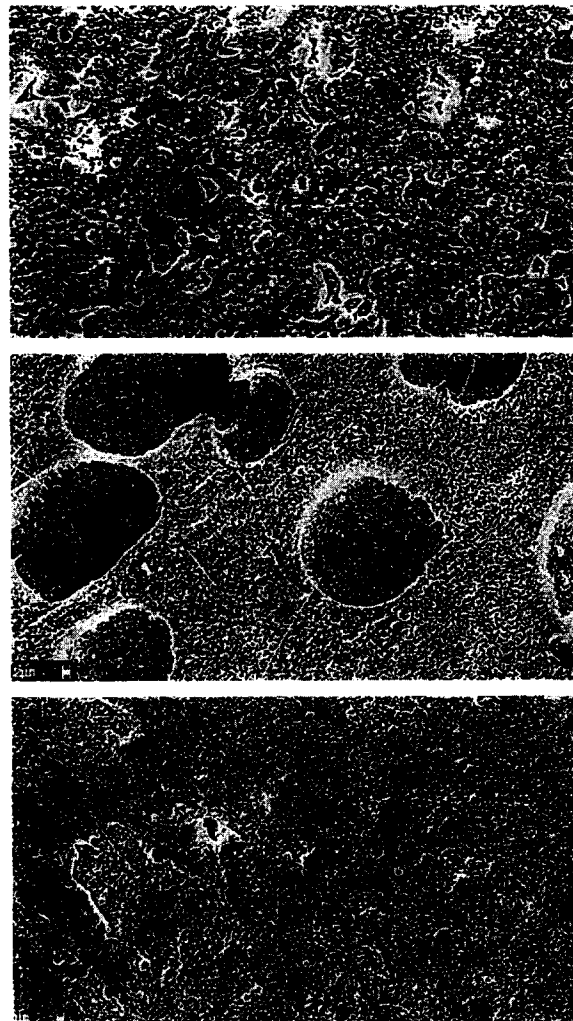


Fig. 9. Electron micrographs of the surfaces of microporous separator materials: (a) microporous polyvinyl chloride/silica; (b) phenolic polyester, and (c) polyethylene; magnification $\times 5000$.

ments of high porosity and good wetting are a must for all separators to be used in gelled VRLA cells.

4. Influence of separator surface characteristics in assisting oxygen transport

As discussed above, the movement of oxygen across a microporous separator depends on many factors, mainly: void volume porosity, pore-size distribution and uniformity of the pore structure. Each of these factors contributes to the efficiency at which oxygen as a gas can travel between the battery electrodes.

There is a fourth factor, however, that may be just as important, if not more important. This is, the type of surface that a microporous separator possesses. After all, it is the surface features of the separator that the incoming gas first encounters. The nature of the surface is a key determinant of the extent to which there will be oxygen permeability across the separator. Three categories of separator surface can be defined:

1. low permeability, containing very few small openings;
2. medium permeability, containing an intermediate quantity of openings, and
3. high permeability, containing many openings and of various sizes.

In order to examine surfaces at close proximity, it is necessary to resort to scanning electron microscopy (SEM). Fig. 9 gives electron micrographs of the surface features of microporous separator materials available for use in gelled VRLA cells. The two polymer/silica separator materials should have similar surfaces, dominated by the presence of silica agglomerates, both large (10–20 μm) and small ($< 1 \mu\text{m}$). This does not happen, however, since the type of polymer and the method of its use are very different. The polyethylene polymer (Fig. 9(c)) is melted over the silica agglomerates and, thereby, almost totally smothers them and allows only very small openings that are randomly distributed across the surface. The polyvinyl chlo-

ride polymer (Fig. 9(a)) is not smeared over the silica agglomerates. It leaves their outer surfaces free and produces a great variety of openings, from the sub-micron to the micron size range. The phenolic resin/polyester (Fig. 9(b)) exhibits large openings, but its surface even inside these openings is dominated by the sub-micron pores of the cured resin grains. From such an analysis, it is clear that the best chances for oxygen transport occur when the separator material exhibits the greatest number of openings.

Since the process of gel cracking is totally random and the size of the micro-channels ranges from sub-micron to micron, it follows that it is very important for the separator surface to match closely this pattern. The sketches shown in Fig. 10 illustrate this point. Once more is known about the qualitative and quantitative details of gel cracking mechanisms, this visualization of what happens at the gel/separator interface will be further refined.

5. Conclusions

It is clear from the studies reported here, that the separator does play a role in the performance of VRLA cells whose electrolyte has been immobilized in silica gel structures. The separator is not just an obstacle to oxygen transport from the positive to the negative plates during its cycle of evolution at the positive plates and reduction and water regeneration at the negative plates during the charging process.

Oxygen permeability is an important characteristic that is highly dependent on the porosity of the separator. Low-permeability separators do not allow the passage of oxygen until very low electrolyte saturation levels are achieved, whereas high-porosity separators with high permeability allow passage of oxygen at relatively high saturation levels.

Different gel-generating techniques in VRLA cells result in different types of gels. They can be roughly categorized as going from a 'soft' (low silica content) gel to a 'hard' (high silica content) variety. These will be correspondingly easier and harder to crack.

The type of separator to be used in each type of gelled VRLA battery application has to be carefully considered. Besides the universal requirement of high porosity, (at least 70%) and high wettability, the separator must have an optimal pore-size distribution and a type of surface that will give best results.

In general, much more has to be learned not only about the impact of the separator on the performance of the gelled VRLA cell, but also about the behaviour of the gelled electrolyte throughout the life of the cell. By virtue of such research, both items could be better integrated into a well-functioning, key component of the valve-regulated lead/acid cell.

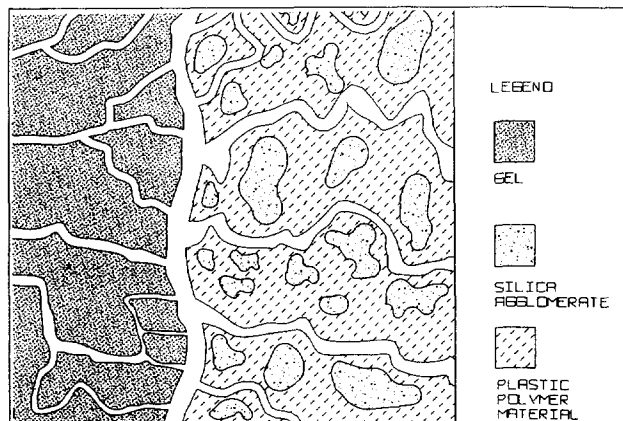


Fig. 10. Visualization of how gel micro-channels can match with the separator micro-surface openings.

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