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Handling Sulfidation

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Solvay Specialty Polymers markets an extensive family of sulfone polymers: Udel® polysulfone (PSU), Veradel® polyethersulfone (PESU), Radel® polyphenylsulfone (PPSU), Acudel® modified PPSU and Duradex® PPSU. These high-performance amorphous resins provide exceptional properties: thermal stability, sterilizability, stress-crack resistance, transparency and ease of processing.

Occasionally, end-users encounter the presence of black specs or streaks within parts molded from products within these families. There can be numerous causes for these defects:

- Degraded resin
- Contamination
- Burned particles
- Sulfidation
- Equipment damage or wear

Although specks and streaks caused by any of these five factors are similar visually, the mechanism that creates them is very different for each one. Of those listed, sulfidation is by far the most complex and challenging. The purpose of this document is to give you some background and guidelines on how to reduce this defect when it is related either totally or in part to sulfidation.

Information concerning degradation, contamination and equipment damage is available through Solvay's technical service department.

NOTE: Before taking any action, an experienced professional should confirm that sulfidation is occurring. An accurate diagnosis can save significant amounts of time and resources.

Defining Sulfidation

Sulfidation is the creation of iron sulfide on the inside of the injection molding machine screw/barrel assembly and/or within a hot runner system. Sulfidation is a chemical reaction (noted as Fe + S = FeS) that occurs whereby unprotected steel reacts (at processing temperatures) with sulfur that's liberated during the processing of sulfur containing polymers. This reaction produces a very thin, brittle film of iron sulfide (deep black in color) on the surface of the steel which is easily removed by injection pressure. The thin, black film that's removed is pushed (or injected) into the molded part, causing the following:

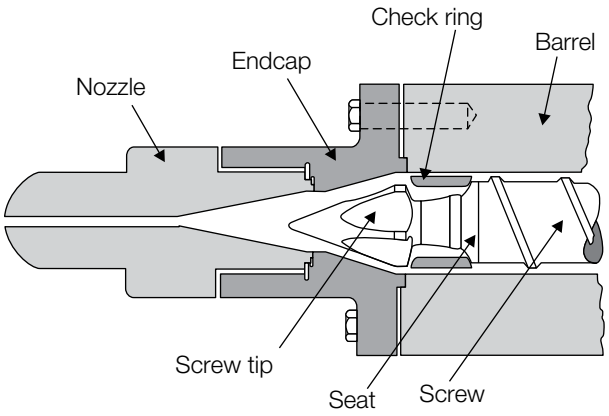
- Small black "chip-like" specks inside the part (type a)
- Thin grey or light black "smoky" appearing traces (type b)

The images in Figure 1 show how sulfidation black specks (type a) and streaks (type b) look in a molded part. Both types can be present at the same time. In colored resin, sulfidation defects manifest themselves more often as type b.

Figure 1: Examples of sulfidation black specks and streaks

Sulfidation particles are very brittle. They break easily and have very sharp, well-defined edges. A trained specialist understands that these particles are formed as a surface coating inside the injection unit. They break off from the surface and are injected with the melt, causing black "chips" that are perceived as specks when seen in a molded part.

Figure 2: Screw and barrel comoponents



Diagnosing Sulfidation

To efficiently resolve the problem of sulfidation, it is extremely important to identify where in the injection group (i.e., which area in the screw and/or barrel) the reaction is occurring. A conventional injection molding machine contains seven screw and barrel components which are detailed in Figure 2.

Sulfidation source identification must be performed on a machine that has processed a sulfone prior to examination. In this way, sufficient deposits will be present for easy identification during disassembly.

Typically, the process of addressing this issue is as follows:

- Isolate and/or identify specks or streaks in part
- Determine where in the process equipment sulfidation is occurring
- Identify why sulfidation occurs at the places identified
- Exclude all processing deviations as a potential cause
- Consider upgrading deficient injection components

Diagnostic Procedure

As mentioned earlier, the zone producing sulfidation particulate should be identified. In the case of an injection process using a hot runner system, identification will require an evaluation of the injection group and a separate evaluation of the hot runner system.

A quick aid in determining whether sulfidation is occurring in the injection molding machine is achieved by purging the injection molding machine using barrel temperatures identical to what would be used during normal injection molding.

The extrudate should then be very closely examined with the aid of a handheld magnifying lens (5 –10x). If sulfidation is occurring within the molding machine, small characteristic particles will be present in the purge material.

Determining whether additional sulfidation is occurring in the hot runner system (if presence of sulfidation has already been identified in the molding machine) is more difficult. In most cases, it will require the help of an experienced technical person. If no sulfidation is occurring in the molding machine, the same purge procedure should be performed with the mold containing the hot runner being open in order to determine if any streaks or specks are being produced within the hot runner.

The injection group (barrel screw, check ring assembly, nozzle, etc.) should now be disassembled in order to confirm exactly which components in the system are causing sulfidation residue. Remember, visual descriptions differ widely from one individual to another. The purpose of this exercise is to identify where sulfidation is occurring, not degradation.

It should be noted that sulfone polymers, when cooled to room temperature, are extremely strong, and withdrawing the screw from the barrel will be extremely difficult. Purging with a small amount of polyethylene prior to disassembly of the screw will make it much easier to pull the screw out of the barrel. Brief purging will not normally affect areas where sulfidation has occurred.

The disassembled injection unit should be placed on a bench, where there is adequate light to evaluate the nature of the discolored or blackened sulfidized resin on any of the components.

Care should be taken to separate the blackened deposit from the metal surface. Sulfide particles are composed of sulfur that has chemically combined or reacted with the iron, creating iron sulfide. Iron sulfide is slightly magnetic, very brittle and deep black in color. At this point, a small hand-held magnet will be very helpful. Final confirmation may be made by a qualified laboratory for elemental analysis. Dark brown and non-magnetic deposits are almost always associated with degraded polymer, not sulfidation.

Components where sulfidation is present should be evaluated with the assistance of an experienced injection equipment manufacturer (not Solvay).

Preventing Sulfidation

Sulfidation occurs when iron present in the injection unit steel components reacts with free or liberated sulfur generated by the injection process. Strategies to prevent this are listed below in order of increasing cost:

- Reduce sulfur liberation via a less aggressive process
  - Avoid excessive melt temperatures
  - Avoid long hold-up times
  - Use moderate back pressure
  - Use moderate screw dosing speeds
- Avoid sulfidation by improving cleanliness of the injection group
  - Frequency of the cleaning and purging steps (more is better)
  - Completely remove degraded material using nonabrasive tools
- Upgrade process components via changes in metal composition or more specific selections when ordering an injection group.

Purging Procedure

Sulfone polymers can be purged from processing equipment by a variety of techniques. Because these sulfone resins are tough, stable, high-temperature materials, the most effective purging procedures replace the sulfone resin with a lower temperature plastic that is more easily removed. Typically, the recommended purging material is polyethylene, but suitable commercial purging compounds can also be used.

The most effective procedure is a step-wise temperature reduction while purging with a fractional melt-flow, high-density polyethylene. When finished molding with sulfone polymers, the machine should be slowly run dry of material while the temperatures are brought down to around 316 °C (601 °F). When the barrel has run dry, introduce the polyethylene and purge until no sulfone resin is evident in the melt patty. At this point, reduce the machine barrel temperatures to around 288 °C (550 °F) and allow the material to sit in the barrel for several minutes, then purge dry the polyethylene and pull the screw for final cleaning if needed. Temperatures can be lowered for shut-down or setup for the next material.

Screws, barrels, check valves, etc. are composed of high-performance steel alloys. Steels may be modified or alloyed to improve their ability to resist chemical attack or oxidation by adding elements such as chrome, nickel, molybdenum, cobalt, etc. Experience has shown that injection components containing at least 20 % chromium or an additive package based on Stellite® can dramatically improve corrosion and chemical attack. The use of highly nickel-based alloys should be avoided. It is advisable that the molder contact a professional screw and barrel supplier to obtain recommendations as to what steel solution is best adapted to their injection equipment.

NOTE: Solvay manufactures injection molding resins. The content of this document is meant to inform those who wish to gain a better understanding of sulfidation. This information is offered as a suggestion, but not as a guarantee of success. Remember, sulfidation may only be delayed by good steel composition. Inadequate cleanliness in an injection machine can slowly encourage the appearance of sulfidation. We suggest that those involved work with an injection machine supplier using this understanding to the best of their ability.

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