Hot and Cold Cleaning Methods: CO_2 and Nd:YAG Laser Ablation, Sodium Hydride Immersion and CO_2 Cryoblasting

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Introduction

Cleaning of RTM moulds – the problem!

The removal of loosely bound or weakly adsorbed contamination from surfaces can usually be achieved using conventional cleaning methods such as solvents or proprietory aqueous-based cleaning solutions. However, the removal of fully crosslinked material which might be strongly adsorbed or chemisorbed onto surfaces, such as paints or adhesives, presents a much greater challenge. Similarly, residual epoxide resins remaining on the inside surfaces of resin transfer mould (RTM) tooling post curing are strongly adhered to the mould surface and need to be removed so that the mould can be re-used. The mould materials are typically steel or nickel but may be composite-based. Conventional methods cannot fully remove residual epoxide material without the use of hazardous chemicals and mechanical removal can easily result in damage to the underlying mould which may compromise its reuse. Therefore, a number of novel cleaning solutions have been investigated to address the challenging problem of how to remove fully crosslinked epoxide resins from RTM mould surfaces.

Potential Solutions

Laser ablation

One option is to use laser ablation-based cleaning processes based upon either a pulsed CO_2 TEA (transversely excited atmospheric) laser operating at 10.6 μm wavelength or a Nd:YAG operating at 1.06 μm wavelength. To one extent or another all polymers will couple with such lasers so that cleaning can occur via a proposed three stage mechanism. Initially, part of the energy of the laser pulse is simply absorbed by the contaminating resin thereby removing some of the contamination. Secondly, this creates a plasma immediately above the surface which re-radiates energy to the surface creating a secondary cleaning effect. Thirdly, plasma expansion away from the surface generates a shockwave in the opposite direction; once this reaches the underlying metal it causes delamination and further material removal. Note that these three mechanisms are highly interlinked.

The key features of laser cleaning are (a) substrate damage is avoided using fast laser pulses, typically <50 ns, with very high peak power; in this situation the pulse duration is kept shorter than the time required to conduct heat energy from surface to the substrate, and (b) the high reflectivity of the exposed substrate to such wavelengths means the process is “self-limiting” ie. there is little laser interaction with the substrate and little or no surface damage.

For laser cleaning of large mould tools, with typically several square metres of surface area, it is necessary to have (a) a large area defocused beam profile of a few square centimetres (b) an even spatial distribution of energy over the beam profile (c) short pulses, and (d) multikilowatt power lasers to satisfy these requirements. In addition, efficient extraction of ablated material is necessary to avoid recontamination of a freshly cleaned substrate. A comparison of the key features of the two types of laser and their operation is given in Tables 1 and 2.

Fig. 1 shows a nickel mould surface following laser removal of a 150 micrometre thick layer of cured epoxide resin in selected areas. This layer was deliberately applied and cured to simulate the in-service condition. The presence, or otherwise, of residual contamination was monitored by contact angle analysis which demonstrated effective removal of the resin when multiple pulses were applied into the same area. In addition, in cleaned areas, a residue less than 30 nm in thickness was measured by Auger electron spectroscopy (AES) which demonstrated almost complete

Table 1 Features of pulsed CO_2 lasers

Advantage	Disadvantage
Quick cleaning	Purpose built laser design –high cost
Very effective	Complex optics
No damage to tool surface	Requires robotic control
	Isolated cell to treat tooling for safety

Table 2 Features of Nd:YAG laser

Advantage	Disadvantage
Staked systems-small footprint-modest cost	Limited power-can Q-switch to boost power
Simple fibre optic beam guide – manual delivery	Slower cleaning rates than pulsed CO_2
Solid state – high Reliability -safe to use	Slight substrate damage

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Based on presentation given at IMF Symposium on Surface Preparation and Pretreatment prior to Finishing, 14th October, 2008, Birmingham Medical Institute

Published by Maney on behalf of the Institute
DOI 10.1179/174591909X12550821666472

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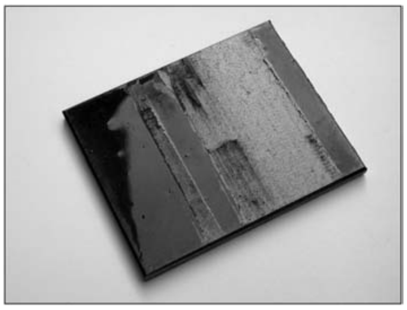

1 Strong absorption of CO_2 laser radiation occurs for thick layers of cured resin resulting in efficient laser ablation. Laser fluence of 8 J cm^{-2} used

removal of the initial 150 micrometre film using CO_2 laser ablation.

Using the Nd:YAG laser the incident energy appeared to be weakly absorbed by a 40 micrometre thick epoxide film on a steel mould which had been introduced to simulate real-life contamination. The mechanism of removal in this instance was predominantly by detachment following cohesive failure of the possibly hydrated metal oxide- see Fig. 2. XPS showed iron oxide to be present on the underside of the detached resin.

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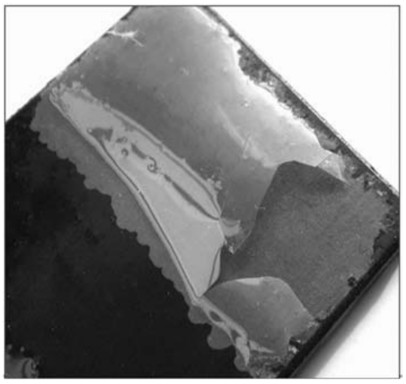


2 YAG laser energy is weakly absorbed by 40 µm thick cured resin. Mechanism of removal is predominantly by detachment since the metal oxide interface preferentially absorbs the laser energy and breaks down. XPS shows metal oxide to be present on the underside of the detached resin

Although laser ablation is considered a "dry" process, as previously mentioned, care must be taken to deal with the emitted material. Also of importance is the capital cost of equipment. In short, the faster the required cleaning rate and the larger the component area the greater is the cost. Importantly, results show laser ablation to be to be very effective in cleaning fully crosslinked resins from metal mould tooling. The ablation process is quite complex and it is highly dependent on substrate and contaminant properties. One major limitation, however, of laser cleaning is that due to their similar chemistries it is very difficult to clean contaminating epoxide material from composite tooling without substrate damage. For this reason, other cleaning processes have been evaluated.

High Temperature Cleaning using a Sodium Hydride Fused Alkali Bath

This process was developed by DuPont (1942) to remove oxide scale and sand residues from castings. It uses a fused alkali bath operating at 360°C through which hydrogen is bubbled. Samples are immersed in the bath, typically, for one hour. The process will clean complex shaped metal tooling, and it is an extremely searching process, being capable of interrogating blind holes and complex geometries.

Again, AES was used to determine the amount of material which was residual following sodium hydride treatment – see Fig. 3. In this case a 150 micrometre thick layer was previously present to simulate the crosslinked epoxide contaminant and this was again seen to reduce to a few tens of nanometres in thickness. A water contact angle of 32° was measured from this surface. A macro image of the previously contaminated, then sodium hydride cleaned and washed nickel tooling is given in Fig. 4. Fig. 5 shows this contaminated nickel tooling before and after removal from the sodium hydride bath (Lenton Treatments, Leicester UK). The resin is reduced to black residue which was easily removed by washing.

There are disadvantages associated with the process of sodium hydride cleaning. These include the fact it is a hazardous process requiring experienced operators. It is usually applied to small parts as the parts have to be lowered into the bath. For cost and safety reasons, the process is best suited to parts which can be cleaned off-site.

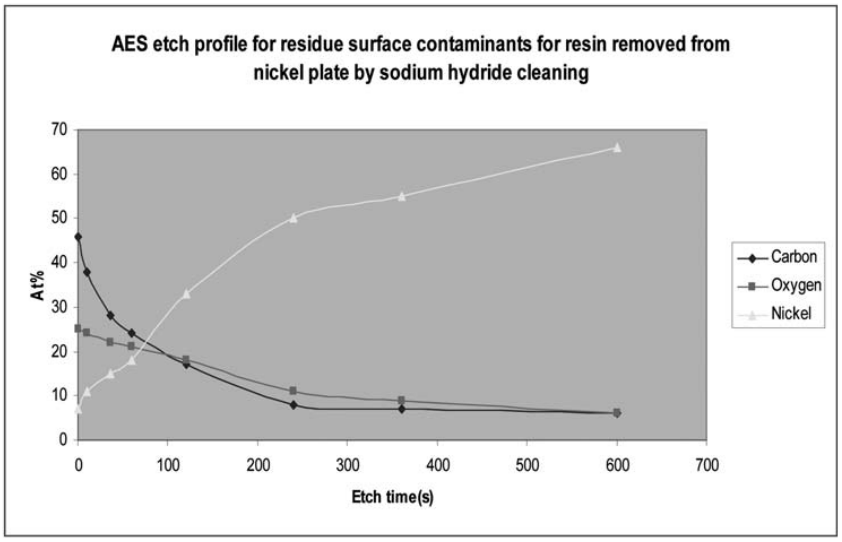
CO_2 Cryoblasting

The cryoblasting process uses solid CO_2 pellets which are accelerated to the workpiece within a stream of compressed air. The cleaning operation is thought to be both physical and thermochemical as CO_2 is known to be a powerful organic solvent with excellent wetting properties. Three principle mechanisms have been observed

(1) Particle impact – the coating suffers mechanical stress as the result of particle bombardment.

(2) Thermal differentials – The coating is cooled by contact with the CO_2 particle. However, this cooling is limited to the surface layer and thus thermal stresses develop in the coating leading to its fracture or delamination.

(3) Molecular expansion – Dry ice cannot remain as a solid when exposed to atmospheric pressure and temperatures. When the accelerated particles penetrate the coating and collide with the substrate, the kinetic energy is converted into heat and the



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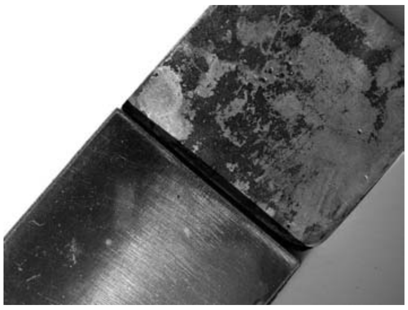
3 Surface contaminants less than 100 nm as measured by AES

4 **Macro photograph of Sodium Hydride cleaned nickel tooling plate (after water jet washing & drying). Water contact angle of 32° measured**



5 **Contaminated nickel tooling before and after removal from sodium hydride bath (Lenton Treatments, Leicester UK). Resin is reduced to black residue and easily removed by washing**

particles sublimate into vapour expanding rapidly- up to 540 times their original volume. This rapid expansion forces the contaminant away from the substrate. Additionally, as the dry ice sublimes, there is theoretically a liquid phase during the accelerated sublimation process whereby all three stages of matter – solid, liquid and gas – are present ie. the triple point.

As both the temperature and pressure rise rapidly, such a liquid phase would provide a very rapid heat transfer from the coating – far faster than to a solid phase – and would allow its rapid percolation into cracks and pores, which would then suffer disruption during gasification.

The cleaning process can be noisy and requires operation in a well ventilated area. The studies carried out to date and case studies reported have been made with the assistance of Cryogenesis Ltd, Sussex UK.

Preliminary studies have shown that, as well as very effectively cleaning metallic moulds, dry ice cleaning can also be applied to composite tooling.

In addition, the compressed air employed to drive the particle to the surface can be heated thus accelerating the sublimation process and preventing the formation of surface condensation.

The cryoblasting process variables which are important include: operating pressure, time, pellet size and the temperature of the targeted surface. Cryoblasting efficacy is further enhanced if the targeted surface is hot.

The key advantages of cryoblasting for this application are that as a process it is easy to operate and it can effectively clean metal moulds with no significant damage to the tooling. Waste is minimised to only the material that has been removed. The process can be used on composites but it needs careful control of particle size, pressure and duration of treatment to avoid damage. There are, of course, a large number of other applications of CO_2 cryoblasting, apart from mould release, including the cleaning of industrial plant and machinery, for example, printing presses where organic contamination is particularly severe. It is also an excellent method of preparation for NDT (Non Destructive Testing).

Concluding Remarks

In addition to the rather time-consuming and potentially disastrous mechanical abrasion methods there are a number of other cleaning options available for the removal of fully crosslinked epoxide resins from surfaces. In this article we have examined very briefly three such options (i) laser ablation with CO_2 and Nd:YAG (ii) high temperature cleaning with a sodium hydride fused alkali bath, and (iii) CO_2 cryoblasting. All were demonstrated to be effective in this role although all have their specific advantages and disadvantages. For a particular cleaning situation the chosen method will depend on:

- Type of contamination
- Substrate material
- Degree of cleanliness required
- Available plant or facilities
- Health & Safety and/or Environmental issues
- Cost