Biofilm Resistance: The Necessity for Hygiene Coatings

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Summary
Hygiene regimes in hospitals, restaurants and many other areas are frequently recognised as being capable of improvement. In these circumstances, coatings for walls, ceilings, floors and equipment can benefit from specially formulated hygienic coatings. However, these require re-examination in the light of recent severe restrictions on biocide incorporation.

This article examines the potential market size and the problem areas. It suggests examination of alternative techniques such as easy clean, design of coatings and cleaning agents in tandem, metal ion incorporation and the use of pollution destroying, antimicrobial photocatalytic titanium dioxide systems. Also the development of advanced surface analytical techniques to detect and quantify contamination at the earliest stage is highly recommended.

In moist open environments, applied coatings are vulnerable to microbial surface colonisation and with potential biodegradation of the coating and substrate. Microbial spoilage is estimated to cost the EU, 20 - 25 bn Euro p.a. Microbial biofilms may be reservoirs of bacterial and fungal contamination which, on surfaces in areas such as food processing and hospitals, can create dangers to health.

Bio-Contamination of Surfaces - The Size of the Market and the Problems
The United States demand for disinfectant and antimicrobial chemicals is projected to reach 135,000 tonnes , valued at U.S. $700 m by 2005 from over 50 suppliers of which four account for almost 50%.

If we consider Northern Europe as similar to the USA in requirement with an equal or perhaps greater need for biogrowth inhibition in the hot and humid climate of much of the rest of the world, we can probably triple those estimates in order to derive a global figure of 400,000 tons valued at $2 billion.

The USA estimates assume the paint and coatings market to be the largest consumer for antimicrobial additives - U.S. $229 m. We might, therefore, project a global figure for antimicrobial additives for coatings that may reach about U.S. $700 m by 2005. These values pale into insignificance if compared to the cost of remedial actions rising from the consequential problems created through careless hygienic practices.

The issue of hygiene is especially critical to contact surfaces within:

- The food processing, supply and catering chains
- Health and medical establishments
- Animal husbandry
- Water and Sewage Operations
- Domestic situations
- Heating, Ventilation and Air Conditioning systems

We know that few surfaces are bacteria-free. Biofilms on tiled areas can still support microbial growth. Silicone sealants are representative of materials with a particular need of incorporated biocides. Stainless steel producers are actively seeking anti-bacterial measures.

The driving forces which are pushing in the direction of ultra-hygiene are powerful and irresistible:

- Greater consumer awareness
- Positive legislation for health
- Negative legislation to restrict biocides
- Legislation to restrict aggressive cleaning compounds
- Legislation to restrict biocidal agents/systems
- New functional raw materials
- Easy clean requirements
- Need to reduce increasing contamination/infection
- Potential to design surface coating and cleansing systems in tandem.
- Increased use of pre-cooked food
- Expansion of fast food outlets.
- Down time costs in the processing chains
- Potential to develop easier, speedier and more economic recoating techniques.

Super hygienic surfaces

Though surfaces may look clean we are aware that all available areas, including our own skin and objects we handle, such as money, credit cards and door handles will have a vast number of unseen microbes colonising the space. This is especially true of surfaces in the fields of animal husbandry, the food chains and health complexes or wherever people accumulate in close proximity. Attempts to use disinfectants of various types and strength appear at best, to offer a hope of destroying “99% of germs”. Even if this were true the surviving 1% would quickly breed to refill the available niches and we have thus accelerated the development of resistant coatings.

How then can a strategy be developed to cope with the working surfaces, walls, ceiling floors and so on in such diverse locations as:

- Hospitals
- Catering Establishment
- Sports Centres and swimming pools
- Care Homes
- Offices
- Schools
- Institutions
- Food Chains
- Food Producers
- Food Storage
- Kitchens
- Bathrooms

In animal husbandry and food supply chains, we know that we are faced with serious, expensive and politically sensitive problems arising from infections such as BSE, swine fever, foot and mouth disease, salmonella, listeriosis and many more.

Sickness, due to food contamination, is increasing. A recent report suggested 4 million cases of food poisoning from poor hygiene in restaurants in the UK alone and this is probably understated, not only for virulent new strains of bacteria contamination such as E. Coli 157 but also for much under reported "milder stomach bugs which debilitate for 24 hours or so". Some of this may be due to modern practices of using prepared frozen foods cooked too quickly in the microwave and to the assumption that "food does not deteriorate or cross contaminate in a refrigerator". A contributory factor may also be poor personal hygiene such as inadequate hand washing (and worse) as well as the assumption that a rapid spray and wipe of surfaces with a proprietary anti-microbial is adequate.

This complex series of hygiene problems may be difficult to resolve but a start can be made through the development of hygienic coatings based on novel concepts and designer cleaning systems.

Performance Factors which need to be considered in this respect are listed below:

- Durability
- Retention of Activity
- Minimal degradation of surface characteristics and appearance
- Resistance to:
    - Heat
    - Chemicals
    - Solvents
    - Fats/Oils
    - Staining
    - Scratching
    - Water
    - Steam
    - Sticking
    - Cleaning Agents

A larger list of challenges to researchers becomes apparent by considering the ideal properties required from a Hygienic Coating**:**

- Flexible
- Tough, hard surface - anti scratch, non scuff, mark resistant
- Abrasion and chemical resistant - non flaking
- Non-toxic
- Minimal odour
- Non leaching/migrating
- Smooth, non-porous
- Insect repellent
- Easy clean
- Easy recoat/touch up

- Sterilisable
- Stain/oil/dirt/water/steam/detergent resistant
- Heat resistance - to avoid cracking and flaking
- Low temperature performance
- No discolouration
- Colour retention (uniform)
- Vapour permeability to allow substrate to breathe
- UV resistance
- Non-slip
- Antistatic
- Slow/sustained/controlled release?
- Anti-condensation

There is a need to understand the principles of bioadhesion
The adhesion of micro-organisms to surfaces is influenced not only by the bioadhesive characteristics of the potential fouling organism but also by the properties of the surface, e.g. chemical composition of the surface, physical characteristics such as surface roughness and by biological features such as the previous presence of a biofilm. Of the physicochemical features, the surface free energy of the substrate is probably the most important. Some bacteria are known to have separate adhesion mechanisms for low and high surface energy materials.

Complex Biofilms*
From the point of view of detection, analysis and eradication, we must not be misled into imagining a biofilm which may form on a wetted surface, as a simple monolayer of one species of active micro-organism but more as a complex ecology reminiscent of a nano-rain forest.

Given suitably moist conditions, bacteria grow in tiny enclaves, which are called micro-colonies. Bacteria themselves generally constitute less than a third of the film, the rest is a "gooey" substance the cells secrete, which invariably absorbs water and traps small particles. The goo - or, more formally, the extracellular matrix - holds each microcolony together. A biofilm is reported to be built of countless such groupings, separated by a network of open water channels.

The fluid coursing through these tiny conduits bathes each congregation of microbes, providing dissolved nutrients and removing waste products. The cells situated on the outside of a microcolony are well served by this plumbing system, but those in the interior are largely cut off. The dense aggregation of cells surrounding them and the organic matrix that cement things together act as barriers to water flow. So the cells inside the colony must make do with the nutrients that can diffuse inward to them. Actually, the supply is not all that meagre: because the glue is mostly just water, small molecules can move through it freely - albeit with certain important exceptions. A substance will have a hard time diffusing to the centre of a microcolony if it reacts with the cells or matrix material it encounters along the way. Aerobic cellular activity and growth take place only where oxygen can penetrate - the outer two or three hundredths of a millimetre of each tiny colony. Deeper down, the cells are alive but dormant. Rather they adhere to various wetted surfaces in organised colonies that form amazingly diverse communities. Microorganisms in biofilms depend critically on their ability to signal one another. At times, antibiotics and germ-fighting cleansers may fail to pierce the film. Other factors enhance tenacity as well. Even where an antimicrobial agent penetrates biofilms easily, the microorganisms often still survive aggressive treatment that would eradicate free-floating cells. Chlorine bleach, a favourite of home and industry, finds it difficult to eradicate biofilms. This reactive oxidant will eventually burn its way in, but first it must deplete, layer by layer, the neutralizing capacity of the film, which takes more time and bleach than one might expect. It is easy, therefore, to be lulled into thinking that all bacteria must be dead when many remain alive.

The safety of drinking-water supplies can be compromised by biofilms, which often grow inside distribution pipes. Protected by a gooey film, disease-causing microorganisms can proliferate despite chlorination. Researchers at Stanford University have shown, for example, that by forming itself into a biofilm, the organism responsible for outbreaks of cholera, Vibrio cholerae, can survive chlorine concentrations 10 to 20 times higher than are normally used to treat drinking water. In 1996 biofilms repeatedly caused the water supply of Washington DC to violate federal standards for bacterial contamination.

* *Source:* *Battling Biofilm*
J.W. Costerton and Philip S Stewart

Understanding the Problem

In order to begin to solve a problem the prime requirement is to know your enemy. This implies that an array of investigative and analytical techniques are required for in-depth identification and analysis before elimination strategies can be developed such as those listed.

Test Procedures

- Hygiene audits
- Contamination tests
- Determination of minimum inhibiting concentrations
- Determination of kill dose
- Bacterial and fungal film testing
- Enzyme detection
- Disinfection testing
- Analysis:
  - contamination
  - bioactives
  - cleanliness

Development of Test Methods

Fungi, such as moulds, yeasts and algae are visible in mass, but it can be advantageous to detect and eliminate them at an earlier stage, when contamination and the consequential substrate deterioration has not yet become obvious.

Bacterial contamination is not usually visible in-situ, so test methods are required to detect unseen biocontamination, including dormant microbes, and, if possible, to identify individual species in cases of multi-species infestation. Modern thin film sensor technology should have this ability using biochemical/DNA indicators.

Need for test method development

- Various approaches exist for hygienic surfaces but their efficacy, under service stresses, is largely unproven.
- Need to detect contamination at a sub-visible stage:
  - essential for most bacteria
  - desirable for fungi and algae
- Traditional approach
  - swab and culture
- Modern Approach
  - DNA profile/amplification
  - enzyme indicator
  - biochemical markers

Development of a series of standard 'biodirt' materials might be a viable method of categorising the effectiveness of sterilents and sterilisation/cleaning procedures.

Easy Clean

An important requirement for a hygienic coating is easy clean. There is little point in producing an effective bioactive film if an inevitable film of oil/dirt /grease/food particles is likely to provide a nutritious barrier layer upon which biogrowth can occur**.** Easy clean may imply an hydrophobic non-stick surface, such as that provided by fluoro-based products. Alternatively an hydrophilic surface may offer ease of wash-off by a continuous flow of water such as might be achieved by siloxal modification. Easy clean is, however, a simple concept since it is also dependent upon the cleansing systems. Highly active cleaning chemicals may be themselves toxic and aggressive and may, with time and repeated applications, degrade the surface and inactivate bioactive systems.

The easy clean concept is only effective if test methods exist to detect and quantify the contaminants. It may be possible to develop an efficient and durable easy clean surface which is designed in tandem with matching cleaning procedures, but even this it is still not enough since some bioactive effect is still desirable. Incorporation of biocides is an obvious route but the range of approved biocides is being severely restricted and may be reduced even further in future. The cost of developing new biocides has become largely prohibitive. Some biocides may not migrate to provide surface replenishment. Biocides capable of migration may migrate out of the film resulting in a lessening of active strength and environmental contamination. Chipping/flaking of paint films could give rise to product contamination. Today it might be wise to consider less dependence on biocide usage or at least minimisation of the rate of addition.

Photocatalytic Coatings and Films

Titanium Dioxide (TiO_2) is transparent and colourless, its refractivity second only to diamond. When TiO_2 has a particle size of about 0.3 micron, the particles refract, scatter or reflect nearly all the incident light and hence appear brilliant white. This is the reason for its extensive use in paints.

When exposed to UV light at 338 nanometres, Titanium Dioxide ejects electrons leaving behind positive 'holes' which attract hydroxyl (OH^-) ions. Formation of hydroxyl radicals results. The active chemical site is instrumental in the disruption of organic material. It is now recognised that the poor durability of some TiO_2 containing coatings could be due to degradation by this photo catalytic mechanism and that the anatase crystal structure is far more active than rutile. Fortunately, most of the highest energy solar radiation is absorbed in the ionosphere. However, 6% of total radiation at ground level lies within the wavelength range of 280 - 390 nm. Conventional TiO_2 photocatalysts are active at about a 360 nanometre wavelength which results in use of only 3% of total solar energy. Visible light activated systems might use about 30% of the solar light energy.

By absorbing ultra-violet light, specially developed anatase can oxidise organic compounds at room temperature. Thus, it has the potential to decompose dirt, grime, atmospheric pollutants and VOC as well as destroying micro organisms. These properties can be triggered by very low fluxes of UV photons generated by sunlight, fluorescent/incandescent lighting and, in some cases, by visible light.

The effect is generated by loss of oxygen atoms from the TiO_2 with reduction of Ti_4 sites to Ti^3 sites which can attract hydroxyl groups to create hydrophilic region with oleophilic domains. In the absence of UV light TiO_2 coated surfaces exhibit hydrophobic characteristics but when exposed to UV radiation the surfaces switch to a combination of hydrophilic and oleophilic states. These combinations provide opportunities to develop ‘self-cleaning’ surfaces. Glass surfaces treated with TiO_2 films and then exposed to UV-light becomes highly hydrophilic. This effect diminishes with time in the dark but is quickly reactivated by re-exposure to UV. This may open the way to alternating hydrophilic/hydrophobic properties offering repellency, self-cleaning and easy wet-view auto windscreens.

R&D work is required to identify the most appropriate physical form, deposition/incorporation techniques and the resin system yielding the greatest durability. Selection of the most active and durable grades under given circumstances will be critical.

Potential Novel Techniques (alone or in combination)

- Silver ion incorporation
- Photocatalytic titanium dioxide
- Silicone quarternary ammonium compounds
- Sacrificial coatings:
    - alkali soluble
    - strippable/recyclable. Strippable films may provide an answer in some circumstances, especially if the stripped material can be recycled. Alternatively a strippable film, somewhere between a sheet of sellotape and a ‘post it’ note with an indicator incorporated could perform valuable service. A water soluble sprayable coating incorporating detection agents might be used to indicate where contamination exists and might also remove contamination when stripped.
    - multi-layer film
- Fluoro/Silicon containing resins
- Dry paint film:
    - additive coated
    - additive incorporated
- Incorporation of cleaning agent activators
- Design of surface and cleansing system in tandem
- Tuned Ultra violet
- Ultra sound
- Ozone

Conclusion

There is an urgent need for improvements in hygienic surfaces and it is vital that high quality and speciality functional coatings are used in conjunction with stringent cleansing regimes. With time, dirt build up on any system may negate anti-microbial characteristics and create potentially dangerous contamination conditions. Research is required on a variety of synergistic approaches as identified in this article. In the never ending, and constantly escalating, war against bacteria and other contamination, we can make a difference and enhance the caring image of the coatings industry.