Hygienic coatings: The next generation

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Summaries

Hygienic coatings: The next generation

Hygienic coatings can be formulated both to provide ease of cleaning and to incorporate active ingredients which assist in the removal or deactivation of biocontamination. Such coatings systems can play an important role in restricting the spread of microbiological contamination. Hygienic coatings must withstand severe conditions, and their development and market growth are likely to depend on a range of emerging technologies such as photocatalysis, dendrimers, and fluorinated and fluorosilicone compounds.

The nature of microbiological contamination and routes of transmission are reviewed and the market areas and design factors for hygienic coating systems are outlined with specific attention to some novel ingredients and technologies.

Revêtements hygiéniques: La prochaine génération

Les revêtements hygiéniques peuvent être formulés de manière à offrir la possibilité de nettoyage facile tout en contenant des ingrédients actifs qui aident à enlever ou à déactiver la biocontamination. De tels revêtements peuvent jouer un rôle important dans la limitaton de la progression de la contamination microbiologique. Les revêtements hygiéniques doivent résister aux conditions sévères et leur evolution et la croissance de leur marché dépendront probablement de toute une gamme de technologies naissantes telles que la photocatalyse, les dendrimères, et les composés fluorés et de fluorosilicones .

La nature de la contamination microbiologique et les routes de transmission sont examinées. Les secteurs appropriés du marché et les facteurs de design qui sont impliqués dans les systèmes de revêtements hygiéniques sont expliqués dans les grandes lignes. On a prêté une attention particulière à quelques nouveaux ingrédients et technologies.

Hygieneanstriche – die nächste Generation

Hygieneanstriche können sowohl müheloses Reinigen als auch die Entfernung oder Neutralisierung von Biokontamination wie Bakterien ermöglichen. Solche Anstrichsysteme spielen eine wichtige Rolle wenn es darum geht, die Ausbreitung von Mikroben oder Bakterien zu verhindern. Hygieneanstriche müssen widerstandsfähig sein. Die Entwicklung der Anstriche und der Wachstum des Marktes hängen von einer Reihe von neuen Technologien ab, wie zu Beispiel Fotokatalyse, Dendrimere, und fluorinierte Verbindungen und Fluorsilikate.

Die Arbeit beschreibt die Arten von mikrobiologischer Kontamination und die Übertragungsweise, sowie Marktnischen für Hygieneanstriche und Designvorgaben für Anstrichssysteme, insbesondere mit bezug auf einige neue Wirkstoffe und Technologien.

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Introduction

This is an age when we believe we are familiar with infective dangers but are instead confused by a deluge of misleading information about the true threats arising from micro-organisms. Under the right conditions, ten germs can multiply to ten million in a matter of hours. Some of the conditions of modern life seem designed to positively encourage the spread of micro-organisms. At the same time, the use of biocides and the selection of active materials used in them is coming under much closer scrutiny.

There is therefore a real need to provide surface modification methods that play a part in the never-ending, constantly escalating and vital fight against hostile micro-organisms. We are seeking to develop surface finishes that make it simpler to maintain hygienic areas. The concept we call 'hygienic coatings' should really be considered a shorthand for 'durable surface modification for ease of sanitation', as we cannot confine the subject only to liquid paints nor to obvious surfaces such as walls and floors. Really, what we wish to promote is best described as 'systems of improved cleanliness'.

Hygienic coatings are emphatically not about the massive use of biocidal chemicals but about the development of integrated, selective regimes designed to minimise biohazards in health care, in the whole food process from farm to fork, and in environmental disposal. Indeed, whilst hygiene and sterility are important in certain contexts, the human immune system may need some exposure to hazards in order to develop. For this reason we seek to contribute towards the development of safer inhibition systems via a culture of thorough cleanliness, with minimal use of environmentally-unfriendly chemicals, and an emphasis on novel approaches and technologies.

We do not claim that hygienic coatings will prove to be a universal panacea for micro-organism-based contamination and diseases. We do, however, suggest that well formulated coatings are an essential contribution to health and safety. The basic requirements are similar to those of a superb coating for many other applications. Such coatings will not be cheap but will prove cost-effective. Rapid, reliable tests are also needed to indicate, identify and quantify the contaminates and microbial deposits present prior to cleaning and the effectiveness of subsequent cleaning.

Obviously, there is a vital need for extensive research and development (R&D) to develop the rules for effective formulation and operation, and this demands collaboration between all sectors of the hygienic chain. It is for this reason that the Paint Research Association has set up a Hygienic Coatings Special Interest Group with its own website at www.hygienic-coatings.com.

This paper will set out to explore and define the need for hygienic coatings, their scope, market potential, key components and some of the many areas for further research.

The global need for anti-microbial weapons

The Black Death, transmitted in overcrowded, unhygienic city conditions, wiped out 30% of the population in Europe. Today's trade routes stretch farther and travel is faster. Paradoxically, these trade routes are also more intimate due to the huge populations occupying our overcrowded, 24-hour-a-day trading societies.

Major highways deliver potentially dangerous infective agents into the Brownian motion of a seething population. Overcrowded public transport, recycled air in aircraft, handshakes, the exchange of money and credit cards, may all contribute to cross-infection for lethal diseases.

We should not underestimate the scale of the problem. Nearly 50,000 people die every day from infectious diseases – about one-third of deaths from all causes worldwide. Diarrhoeal diseases, including cholera, typhoid and dysentery spread chiefly by contaminated water or food, kill over three million individuals annually – and most of the victims are children. Tuberculosis kills another three million people annually, mostly adults. Measles and hepatitis B infections kill more than one million people per year. Even intestinal worm infections kill more than 130,000 people each year.

Worldwide, the losses in terms of human life, productivity and medical costs resulting from infectious diseases are staggering, and the number of virulent and drug-resistant infectious organisms continues to rise. Thus, there can be little doubt that improved and innovative products are needed to control the spread of disease-causing bacteria, fungi, algae, yeasts and viruses. We ultimately have only two choices: to become immune, which is normally achieved by allowing up to 30% of those with low immunity to die, or to ensure that good hygienic practices are built into our culture, though not so good that we discourage the development of immunity.

Cleanliness is next to Godliness

Cleanliness is not primarily about biocides, nor even about coatings, important though they are. The first issue is psychological. If you walk into an area where the floor is covered in discarded cigarette packets and general litter, you will have no hesitation in discarding your own spent cigarette or sweet wrapper. If that same area is pristine, you will be reluctant to be the first to contaminate it. A clean surface is also essential to signal dirt build-up and encourage frequent supervised maintenance. We need to be tough on grime – and the causes of grime.

Of course, avoiding dirt build-up will also have the benefits of denying bacteria nutrient patches to colonise and avoiding the passivation of biocidal action by layers of dirt. It is not sensible to encourage colonisation by harmful micro-organisms with a lackadaisical attitude to cleansing and hygiene. Nor is it sensible to assume that careless and indiscriminate usage of aggressive chemicals claiming to kill 99% of germs will ultimately do anything more than leave untouched pockets of contamination and hasten the development of resistant species, creating an even more hazardous environment. Cleaning removes 90% of contaminants and it helps – but beware the 10% and their offspring.

The consequences of allowing dirt to accumulate are:

- ageing accelerates;
- appearance deteriorates;
- biological colonisation commences;
- more dirt is attracted;
- psychological 'why bother to clean' attitude evolves.

We are faced with severe restrictions on biocides with even more stringent regulations in future. The financial barriers to developing new biocides and gaining approval are now very high, so we want to use only a few of the safest and most effective (and this may be a contradiction) and to use as little as possible so as to gain maximum, long-term, effectiveness.

One definition of a hygienic surface is one with an easily cleaned, smooth, unbroken surface which does not allow the growth of fungi and bacteria, specifically *Staphylococcus Aureus*. Edges and back areas should be fully sealed with a waterproof hygienic filler or sealant.

However, regular wear can result in changes in surface roughness. Cleaning efficiency is related to the degree and type of soiling, substrate topography, the cleaning agents and the process used. The cleaning of surfaces in contact with food requires removal of both food soiling and micro-organisms, but there is a significant difference between actual and apparent cleanliness especially when bacteria and biofilms invisible to the naked eye are beginning colonisation.

The scope for hygienic coatings

All surfaces, including walls, ceilings, floors, doors, partitions, cupboards, work surfaces, handles and equipment are subject to colonisation by a bewildering variety of micro-organisms, sometimes acting as single species, but more often in an alliance of differing species working in concert to form 'biofilms'. These act like multicellular communities having a certain degree of functional specialisation.

Money, credit cards, air filtration systems and, of course, people themselves are also involved in the biological transfer process. Even when we are healthy, every centimetre of our bodies will be colonised by micro-organisms.

Current and future restrictions on many traditional volatile and migratable biocides, coupled with increased public awareness of contamination problems throughout the food, animal husbandry and health chains, will impact on the demand for and the formulation of hygienic coatings.

Thus, the main driving forces are legislation and consumer demand, whilst the solutions appear to lie with a range of rapidly advancing technologies which can be melded into a potent force for improved surface modification, whether by liquid paints, powder coatings, advanced deposition technologies, polymer surfacing or polymer films. We must also understand the interactivity of substrates with actives such as additives and cleaning agents in order to design safe durable systems with maximum cost-effectiveness. Coatings are just one essential component in a myriad of co-ordinated approaches towards providing a culture of care and cleanliness.

Market potential

The question most frequently asked by paint companies is 'What is the current size and breakdown of the market?' The answer is always the same: 'We don't know!' If you examine any breakdown of paint production or sales into significant categories you will not find the heading 'hygienic coatings'. It is certainly small in comparison with other areas, but it is not the current size that is important but the huge potential that is exciting and potentially highly profitable.

Just imagine all the surfaces in the whole world that could benefit from effective hygienic modification. Consider the total surface area in hospitals and food production and consumption areas alone. Evaluate the potential contract to surface a chain like McDonald's restaurants, with about 28,000 outlets worldwide.

Or again, consider the impact on the global institutional and industrial cleaning industry, a US$20 billion global market. A substantial slice of this is in the hands of major players. Johnson Wax recently paid US$1.6 billion to purchase Diversey-Lever from Unilever. It will now have sales of $2.6 billion, representing about 13% of this market. Its prime competitor, Ecolab, which bought out Henkel from their joint operation, now controls about 17% of the market. Think, too, of the effects of future litigation on organisations which have not followed sensible and comprehensive hygienic practices.

Finally, apparent cleanliness may not indicate actual sterility, so no system will be acceptable unless its surfaces can be quickly characterised as to their state of sterility both before and after cleaning. This requires the development of simple and rapid test methods, *in-situ*, portable, and remote read-out sensors which will monitor and warn on the sterility of particular surfaces and components.

The potential for hygienic coatings is huge and can expand for many years, but it needs to be created by forward-thinking companies working in partnerships to make viable a selection of innovative materials, technologies and ideas. It is our intention, with your help, to try to change this situation and to make hygienic coatings a significant area for the future.

I'm sorry – I don't have any small change

Mark Twain is said to have remarked that he 'loved progress but hated change'. But the field of hygienic coatings is very new, and progress is being 'driven' by change. Some of these key drivers are listed in Table 1 along with an assessment of some of the novel ways we will need to devise to meet the challenges they pose. Change equals opportunity, and collaborative ventures can capitalise on this to develop effective coating systems along with maintenance packages.

Areas of application

The obvious primary areas of application for hygienic coatings are:

- pharmaceuticals;

Table 1: The requirements for hygienic coatings

Driving forces	*Ideal system requirements*	*Ideal coating properties*
• Increased and stringent legislation • Restriction on biocides • Potential restriction on aggressive cleaning agents, disinfectants, surfactants, sterilising agents • Battle between biocides and resistant organisms • Heightened public awareness • Claims for respiratory problems due to contaminated HVAC systems • Improved analytical and test methods • Improved selection of narrow wave-length UV	• Good architecture • Appropriate HVAC systems • Excellent coating system selection • Correct substrate preparation • Careful application • Tailored cleaning regimes • Synergy between components • Monitoring of contamination levels	• Minimise dirt attraction (Antistatic?) • Poor dirt retention (non-stick?) – hydrophobic? • Easy clean – smooth, hard, abrasion-resistant – hydrophilic? • Ideally, self-cleaning – regenerable photocatalytic TiO_2 • Scratch and chip-resistant • Improved durability – abrasion resistance, minimal discoloration, micro-cracking, flaking • Resists germicidal and photocatalyst regenerating high-energy UV radiation • Resists aggressive chemical cleaners (regularly) • Anti-condensation • Contains catalysts which enable use of milder cleaning precursors

- biotechnology;
- medical engineering;
- laboratories;
- hospitals, dental and veterinary practices;
- foodstuffs industry;
- beverage industry;
- sterile laundries;
- shower and toilet areas;
- sports complexes;
- animal husbandry – enclosed areas.

In considering food contact areas, for example, we must include not only all surfaces that are directly exposed to a consumable product or ingredient, but also all indirect surfaces from which splashed products, condensate, liquid or dust may drain, drop or be transported into or onto the products. It is sensible to design coatings which are resistant to dirt pick-up and easy to clean. But even this is not enough, for dust particles are 'space-ships' for unseen bacterial colonists. Coatings alone have little point if we encourage the increase of dirt, bacteria, fungi and the like by ignoring the efficient usage of HVAC (heating, ventilation and air conditioning) systems to prevent increase and deposition not only onto surfaces but into lungs.

HVAC ducts and units themselves may represent inaccessible, invisible reservoirs of contamination from which micro-organisms could be wafted into rooms and deposited on surfaces. Both awkward corners and filters have the potential to accumulate dirt and biofilms. Ideally, antibacterial surfaces, remote sensing systems and possibly internal germicidal ultraviolet (UV) sources should be provided.

The connection between HVAC systems and Legionnaires' Disease is now well understood, but authorities in the USA are becoming increasingly concerned at the potential of HVAC systems for spreading fungal and other spores. One report from California suggests that future health claims related to fungal infections could be comparable with those for asbestos related problems.

The nature of biological contamination

There is no escape

The terms 'microbes'or 'micro-organisms' describe bacteria, viruses, lower fungi and lower algae. Microbes may represent about 90% of the living material on planet earth and might be legitimately regarded as the dominant life forms.

Micro-organisms are ubiquitous both in the environment and within and upon the human body. Even in clean, healthy environments, we inhale 5,000 to 250,000 fungal spores each day. Some sources claim that there may be up to 1.5 million different species of fungi, of which only some 70,000 have been described.

More than one million microbial cells per millilitre are typically found in seawater, hence marine biofouling. (It has been suggested that the defences some marine organisms have evolved against this microbial onslaught might be investigated to yield clues to counteracting biofilm formation.)

Micro-organisms fall on us from the air, enter us with water, food and respiration, are rubbed into our skin and travel on everything we touch. We shed them in wastes, saliva, tears, by coughing, by sloughing skin, and by exhaling. Thousands of germs are native to our bodies, five hundred in the mouth alone. Fortunately, only a few make us sick and most of those die trying.

There is no place on earth that humans can go to avoid them. Even in space there may be no escape, because a host of microbiological stowaways have been recovered from space shuttles. Animals, insects and, of course, humans, can act as reservoirs of microbial derived diseases. Zoonosis, the transfer of disease between species, is probably normal and occurs from man to animal as well as vice versa.

The potential for mutation in bacteria is exceptionally high. It has taken only 50 years for bacteria to develop resistance to antibiotics by rapid reproduction cycles (they may proceed through tens or hundreds of thousands of generations in one human lifetime), by inter-species collaboration in forming complex biofilms, by constant biochemical communication, and through an ability to exchange genetic material to adapt to changing conditions.

Microbes are very versatile with regard to the conditions under which they can survive. Some species can even grow in contact with the powerful disinfectant phenol or tolerate cyanide. Fortunately, the majority are beneficial or innocuous, and disease-causing bacteria are in the minority except where sickness is rife. Even so, when a lone species of bacteria generates symptoms in a host which are regarded as a mild temporary inconvenience, this may be because the host's immune system has developed defence mechanisms from previous encounters or the organism has been attenuated by inoculation or by generations of selective exposure. Even this apparent ineffectiveness may weaken the immune system's defences. Poor hygienic conditions generally do not favour any one microbial species or type, but allow the enemy to collaborate in unhygienic alliances to create a step-by-step siege and possibly the ultimate collapse of immunity.

Evolution has depended upon a compromise between collaboration and synergism with benign micro-organisms in order to fend off the constant and aggressive invasion of hostile species. In this constantly escalating battle we are in danger of defeat unless we muster our defences and operate in a reasonably hygienic environment.

Hand-to-hand combat

If you really think about the cross-contamination that can occur when you meet a friend and offer the traditional method of greeting – it would make your hands shake.

Humans carry and transmit micro-organisms via respiration, human-to-object contact, animal-to-human contact, and very much by direct and indirect human-to-human contact. Direct contact may be intentional in handshaking, embracing and kissing, but also unintentional via overcrowding in transport, meetings and the like. Indirect contact is principally through touch, on touch screens, handles, credit cards and money exchange. The constant circulation and very frequent handling of cards, notes and coins provides a vector for a ping-pong game of pass-the-bacterium.

The person who provides you with food and also handles money may be a problem. Cards and coins may be handled for only a brief instant but may then be stored in warm pockets also containing items such as used handkerchiefs, or in handbags which are home to a cornucopia of objects, some perhaps even left there for months forgotten by their owner.

It is also easy to overlook the potential contamination from handles. It can be demonstrated that it is difficult to wash your hands thoroughly enough to eliminate all bacterial contamination. Even then, you may not avoid touching the handle of the door you have just closed with unwashed digits. Unless doors, cupboards and toilet flushes are 'automatic', contact between hands and handles is frequent and inevitable. Hand contact with toilet seats is a definite hazard. We need photocatalytic coatings on handles and frequent cleansing with anti-bacterial wipes.

Hygienically surfaced doors are commercially available, but probably not similarly treated door furniture. Further-more, there has been little attention to locks and hinges, whose lubricants are generally hydrocarbon and thus a possible nutrient reservoir for biogrowth unless the oil or grease contains an approved biocide.

Capability green

In this constantly escalating battle between certain micro-organisms and man plus chemistry, a lone bacterium is not a significant factor unless allowed to divide into a myriad of clones, prompted by favourable conditions or supported by other species.

Bacteria appreciate a terrain of dirt, oil, grease, fat and water deposits, a fertile world which they can inhabit, dine on and where they can form complex biofilms which increase their tenacity and resistance to removal. A biofilm is not just a monolayer of a single species of bacteria, fungi or algae but a thriving multi-layered, multicultural construction site reaching into the air interface to create a surface of incredible intricacy and functionality.

The deposition of nutrients and moisture encourages the first wave of bio-engineers capable of creating an anchor layer. Bacteria communicate chemically and the message 'foundation established – colonisation possible' attracts the next strata of mucus-releasing types providing the glue required to bond subsequent specialist types with different genetic characteristics and performance capability.

The resulting structure may have the complexity of a city or a nano-rainforest with communication channels, nutrient-rich rivers of moisture, osmotic membranes, and the ability to respond to changing micro-climate and varying foodstuffs, undergoing continual growth as long as moisture and nutrition are available. Under high magnification, this is a magnificent engineering feat which often matches the beauty of Capability Brown's Victorian landscapes. By the time such a biofilm has established itself, it is not possible to eliminate it completely by simple cleaning or even with biocides.

Inadequate physical and/or chemical surface cleaning may inhibit only the upper layer of the biofilm, allowing the dormant interlayer to become active. Incorporated biocides, perhaps passivated by time, cleaning and organic and dirt deposits may not prevent colonisation or may inactivate only the bottom layer of this biofilm, which will retain its bond to the substrate.

Powerful cleaning agents, abrasives and high-energy UV light can combine to remove all traces but cannot restore any microbially-sponsored surface degradation. The best approach must therefore be not to allow a biofilm to develop. The selection of high-performance surface characteristics with functional additives will help but will not negate the need for regular monitoring and regular thorough cleaning regimes. Prevention is always better, and ultimately cheaper, than cure.

Moulds and fungi

Mushrooms are the fruits of fungi. The edible kind may be collected in the wild or cultivated (commercial production in the UK alone runs to some 85,000 tonnes). Mushrooms are themselves subject to various fungal diseases as well as being susceptible to bacteria, viruses and a range of insects. Biocides may be of some help in counteracting mould growth, but complete eradication is impossible and the key to prevention is moisture control, for if mould spores alight on a damp area they can grow rapidly. HVAC systems can be prone to mould contamination if significant condensation is present. Moulds can cause health problems via the production of allergens, irritants and in some cases mycotoxins. Mould growth may also encourage colonisation by other micro-organisms.

The unacceptable (sur)face of the food and health chains

Though hygienic surfaces may not be the most important barrier to food and hospital-derived infection, walls, ceilings, floors, work surfaces and equipment in direct, indirect, accidental or incidental contact are significant factors, especially when associated with inadequate cleansing and disinfection procedures.

Clean, shiny, aseptic surfaces are indicators of hygienic practice, leading to safe food and reduced cross-infection, but sterile surfaces cannot be measured by appearance alone. Dangerous micro-organisms and biofilms are not visible, and benign biofilms may be conditioning the surface for co-colonisation by more harmful species. Harsh chemical cleansers, aggressive disinfectants and germicides may give a false sense of security and face increasing restrictions for safety, health and environmental reasons.

Carelessness is not an option

The need to eat and drink is basic but it also creates hazards, because other species on our planet regard our food and beverages as essential for their own existence, and their concentrated colonisation can be disastrous for human health and life. Sharing is not an option.

Food contamination has always plagued mankind, but today's food production, distribution, preparation and consumption is a globalised 365 days per year and 24 hours per day business, and a significant percentage of product is lost through spoilage. This suggests problems in operating procedures, particularly hygiene monitoring in wholesale, retail and domestic situations.

Almost 50% of the world's population reside in urban areas so the food distribution chain becomes longer and the potential for spread of contamination much greater. Cities also tend to contain a significant percentage of deprived citizens living in poor conditions where hygienic practice may be less stringent. Critical attention is needed to all aspects of handling, transport and storage in the food and health chains.

All chefs should be sterile

The use of 'clean room' technology in the pharmaceutical industry, biotechnology, and manufacture of medical products is a key element for modern production processes. Clean rooms are dust-controlled to a very low level via advanced HVAC and filtration, controlled entry and exit systems, whilst personnel wear white overalls including hats and shoe covers. The cost of ignoring these procedures can be very expensive in terms of reject pharmaceuticals or semiconductor failures.

Of course, the cost of significant failures in food processing establishments could be even more dramatic and expensive in terms of human illness and even death in the case of lethal bacteria such as *E.Coli 157* and the inhalation of fungal spores. The rising incidence of illness from infected food clearly indicates a necessity for improved hygiene measures. Practical commercial kitchens can never meet the ideal conditions found in clean rooms, but these may serve as a guide to the standards to be attained.

At home, matters may be even worse. In spite of the popularity of 'star chef' books and programmes on TV we no longer cook, we often just assemble prepared packs whilst watching, listening and reading. We have lost not only the art of cookery, but the knowledge of how to handle food prior to assembly, in the assembly process itself and after assembly. We often have a misplaced faith in the microbiological cleanliness of the food we buy. We cook inadequately in microwave devices, we mix frozen and cooked foods in refrigerators, we ignore 'best by' dates. We do not set our fridges or freezers at correct temperature nor give them a thorough cleansing often enough. Kitchen walls and surfaces may be covered with a layer of invisible grease and subjected to condensation. We do not clean thoroughly, believing that a quick wipe with disinfecting spray or the use of biocide-impregnated boards will yield protection and compensate for careless hygiene.

Design factors for hygienic surface modification systems

Initial design criteria

The first critical issue for hygienic facilities is the initial design, which should ensure that:

- Contamination is minimised, both internally and from other parts of the building.
- Design and layout permit appropriate maintenance, cleaning and disinfection.
- Airborne contamination is minimised with appropriate HVAC systems.
- All surfaces and materials, particularly those in deliberate or accidental direct food contact, are durable, non-toxic in intended use, have suitable anti-drip facilities, provide ease of maintenance cleaning and ultimate removal/replacement.
- Effective protection is provided against pest access and residence.
- Nooks, crannies, crevices and exposed pipework are avoided.
- Inappropriate unofficial fixtures to walls/doors are prevented.
- Integral curved surfaces are fitted between the base of walls and floors (noting that hygienic hazards may arise later if contaminants seep in and are trapped behind such fixtures).

Coatings design

The first requirement is a high quality attractive finish. Next, the coating should be not only easy to clean but provide excellent resistance to dirt pick-up and retention. Durability and scratch/abrasion/slip-resistance are vital. Coatings should deter, inhibit or kill potential colonising micro-organisms without migration of active agents into the local environment. Finally, the coating system should not create health and environmental hazards on stripping and disposal. Ideally it might also incorporate indicators to reveal contamination. The permutations of properties ideally required by a hygienic coating, summarised in Table 1, may be daunting, but these are also those required for high-performance coatings in many other sectors.

Having developed a superb coating from the point of view of mechanical properties, we now have to add biocidal properties and then clean it regularly and thoroughly. Great attention must be paid to the application of coatings using skilled painters. Similarly, cleaning can no longer be the low technology, low cost, unimportant system that it has often been previously. Regular and thorough cleaning is the most important component of biofouling prevention and removal, but this is often the most neglected area. It may be awarded to the lowest quotation, left to low paid, unskilled workers and carried out outside of normal working hours – thus with no supervision from the managers responsible for hygiene and safety.

The cleaning may involve sterilising agents and/or disinfectants, a rubbing/polishing action with abrasives, chemicals, steam and scrubbing. These procedures cannot and must not be neglected. While the paint may be applied once every five years (if we are lucky), a daily cleaning during that time represents up to 1825 serious chemical attacks on the integrity of the surface. All polishing is abrasive and has the potential to degrade a surface by wear. Liquid disinfecting agents may be aggressive to both the surface and those handling the products, whilst inadequate sluicing may leave residues on the surface.

We have to ensure that cleaning regimes do not degrade the resins nor inhibit any 'active' components. All this implies firstly, that the cleaning components and total regimes must be designed in tandem with this coating, and secondly, that over the lifetime of the system the cleaning process is the more expensive and critical component.

It is worth noting that coatings in a commercial kitchen may face more severe conditions than exterior paints, as shown in Figure 1. This confirms the necessity for very high performance levels.

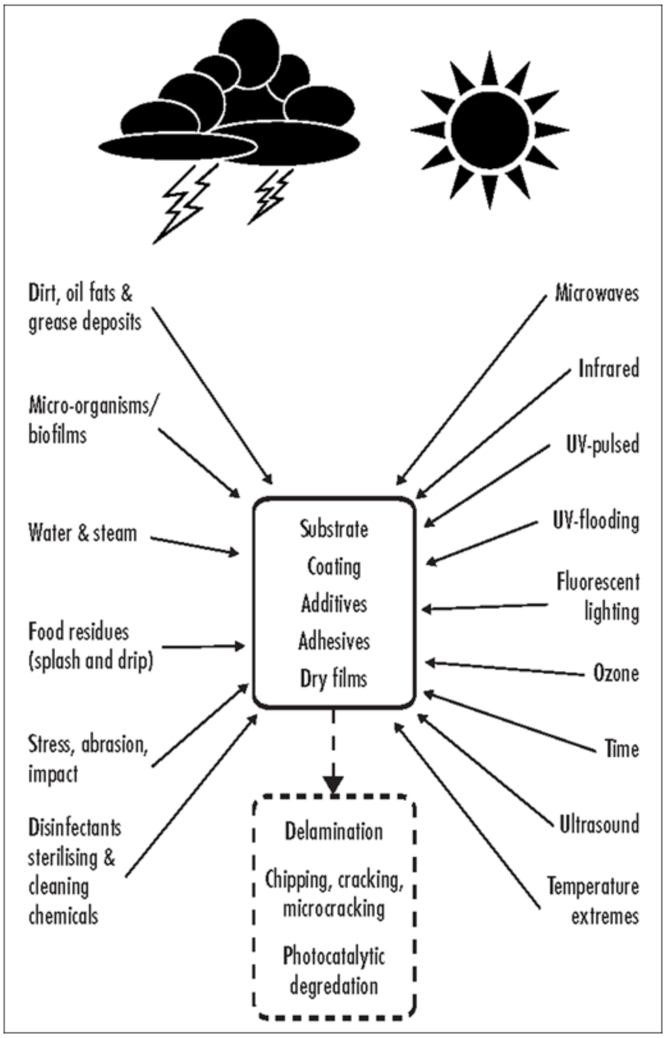

Figure 1: A climate of fear – indoors

Overall, the future need is for novel, innovative techniques such as regenerable photocatalytic coating and high-energy pulsed UV, possibly in synergistic combination with established techniques and compounds applied at lower rates. Investigating the synergisms between selected systems represents a myriad of possibilities for collaborative R&D because a total system in which all components are designed in tandem for effective control is required.

Biocides and surface coatings

Biocides and the biocidal regulations

The worldwide annual market for biocides has been estimated at £3 billion with a growth rate of 4% per annum. However, the market and the materials sold will be substantially affected, at least in Europe, by the Biocidal Products Regulations (BPR). These apply immediately to new active substances and biocidal products based on them. They will also impact on existing disinfectants in the near future. Ultimately, the directive allows ten years for all existing active substances to be reviewed, with possible removal from the EU market, and some will be removed earlier. As many established biocides are being prohibited, with cost barriers to the introduction of new types, it is obvious that a need exists to introduce novel integrated bio-prevention and biocidal systems.

What are antimicrobial pesticides?

Antimicrobial pesticides, such as disinfectants and sanitisers, are intended to disinfect, reduce, or mitigate growth or development of microbiological organisms, or protect inanimate objects (eg floors, walls, industrial processes or systems, water, or other chemical substances) from microbial contamination, fouling or deterioration. This category excludes pesticides intended for food use but does encompass preserving agents in paints, metalworking fluids, wood and many other products.

Antimicrobials are especially important because many are public health pesticides. They include disinfectants used in products for cleaning cabinets, floors, walls, toilets, and other surfaces in medical settings. Their proper use is an important part of the infection control activities employed by hospitals and other medical establishments. Most, however, are classified as hazardous substances, although those for the food and related industries are specially selected. Care is required in their handling, storage and usage, and it is recommended that their use should be eliminated where appropriate. Some products in common use are listed in Table 2. It can be seen that these include some very energetic or highly oxidative systems which may cause rapid degradation of coatings and their components.

The application of biocides

Even biocides incorporated into paint to provide in-can protection for water-based types appear to offer antimicrobial properties for some time. It is known that such biocides may be detected in the surrounding air for up to ten days after application.

One must assume that a conventional biocidal additive, if it is to perform its function for a predetermined period, must be of the migratable type that will continually replenish the surface. It is probable that non-migrating, locked-in types must be washed or worn from the surface or are mainly locked into the bulk of the paint film and unable to perform their designed surface function adequately. So, unless they are exceptionally toxic to micro-organisms, we might question their efficacy, while if they are highly toxic we must be wary of their contamination of the local atmosphere and their safety, health and environmental effects. (Indeed, since this paper was first written, the reinsurance company Swiss Re has expressed the opinion that the trend to incorporate biocides in everything from toothpaste to plastic kitchenware may eventually result in massive liability claims.[1] One such product, triclosan, has been detected in waste-water[2] and in human breast milk, and may give rise to allergic reactions.)

Table 2: Biocidal compounds and their key properties

Chlorine and chlorine compounds	Widely used but must be handled with care
Chlorine dioxide	Can exist in the gaseous, liquid and solid states
Sodium hypochlorite	Effective against free-living bacteria but less so for biofilms
Chlorosulphamate	Penetrates biofilms more easily than alkaline hypochlorite yet less effective as a killing agent
Formaldehyde	Used as a disinfectant and sterilant in both its liquid and gaseous states but must be handled with great care
Glutaraldehyde	A saturated dialdehyde which can be 'activated' by raising the pH value
Hydrogen peroxide	Limited use because of its slow activity and poor stability in complex formulations
Ozone	A stronger oxidant than chlorine and acts faster over a wider spectrum of organisms, leaving no residue on surfaces
Peracetic acid	Rapid action against all micro-organisms. No harmful residues but may corrode some metals unless buffered
Iodophors	Iodine is able to penetrate the cell walls of micro-organisms very quickly
Polyoxometalates	Newly patented materials containing no bleaching agents and employing air as the primary source of oxygen to generate oxidising activity

Novel approaches to biocidal activity

Given the current situation, there is clearly pressure to develop novel biocidal products or systems. Just a few which may be relevant in the context of hygienic coatings or their cleaning may be mentioned here.

- Quaternary ammonium-capped silicones can exhibit a combined tendency to repel moisture and be biocidal. While promising, they may exhibit poor resistance to UV sterilisation procedures.
- The very high pH value of calcium hydroxide can be lethal to micro-organisms on contact. $Ca(OH)_2$ is the basis of limewash. This reacts with carbon dioxide in the atmosphere to form calcium carbonate, which is ineffective as a biocide. However, Alistagen Corporation claims that by using calcium hydroxide 'encapsulated' in a latex membrane along with a stabiliser, its Caliwel paint can retain anti-microbial activity for up to six years.[3]
- Insoluble disinfectants can inactivate, kill or remove target micro-organisms purely by contact, without releasing any reactive agent. Certain cross-linked polymers containing cations or bearing a positive charge on their surfaces have this property; for example, cross-linked ion-exchange resins, quaternary ammonium resins, polyiodide resins and insoluble polyelectrolytes.
- Electrical generation and discharge creates ozone and oxides of nitrogen which are reasonable aerial disinfectants. Underground railways should encourage the spread of infection amongst overcrowded commuters, but in fact the air in the average London tube train is remarkably free of live microbes, probably because of the frequent electrical discharges produced by the trains.

- Some dyes used in the textile industry exhibit antibacterial activity, but their toxicology must be assessed if they are used in novel applications.
- Hydrogen peroxide is employed at concentrations of up to 30%. A combination of only a few per cent concentration plus UV radiation may achieve similar results. This process, in conjunction with photocatalysis, might deserve investigation.
- The concept of using simultaneous exposure to UV radiation and ultrasonic energy in a non-aqueous environment such as air is the subject of a patent.[4] The method is suitable for use in-chamber, in mass production assembly lines, or for air purification.
- In addition to radiation from UV, far UV, pulsed UV, electron beam, microwave and ultrasound, we should not ignore the possibility of antibacterial far infrared systems.
- Compounds of manganese have been used to catalyse peroxygen compounds to higher activity at low temperatures in washing compounds. One such compound was withdrawn after it was found to damage clothes.[5] Ciba is now introducing a different manganese catalyst, said to be effective at only 0.02% addition, and is investigating ways to modify the product for use on hard surfaces and carpet cleaning.

Light cleaning

Photocatalysis

A photocatalyst, in the context of hygienic coatings, is a compound which, after UV, fluorescent or visible light irradiation, exhibits strong oxidation potential via the release of electrons, creating positively charged 'holes' and subsequently hydroxyl radicals. These powerful oxidisers can break down organic pollutants into carbon dioxide and other less harmful components, providing a self-cleaning, deodorising and biocidal surface.

Photocatalysts exhibit reactivity at relatively low temperatures and can be easily 'switched on' or off. The most exciting prospect is that depleted catalysts can be regenerated by UV light and returned to their active state repeatedly. Photocatalytic titanium dioxide already has established uses in air purification, deodorising and catalytic degradation of atmospheric pollutants. In hospitals and other medical-related facilities a potential use exists in nano-air filtration and the destruction of halogenated volatile organic compounds from operating theatres and anaesthetic facilities.

In addition to this, at least two patents have been lodged on the use of dispersions of photocatalytic TiO_2 particles for washing, cleaning and disinfecting surfaces exposed to light. A film-forming dispersion is deposited on the surface and then simply dried.[6]

Types of photocatalyst

The photocatalytic activity of titanium dioxide in coatings was first observed when pigment grades degraded the binding resins. Anatase is far more active than rutile titanium dioxide, and is probably the most effective, economic and readily available material, with performance already proven in a commercial use, though some researchers have suggested the use of mixed systems to provide a wider regeneration bandwidth. Photocatalytic grades of titanium dioxide have been developed in a range of particle sizes, the larger having the normal opacifying power of pigment grades. Other oxides can also exhibit photocatalytic activity and might be used alone or in combination with TiO_2. In particular, synergy may be possible with metals such as silver which have their own biocidal activity.

When formulating coatings containing photocatalysts, techniques must be devised to protect the substrates, binder resins and other additives from degradation by repeated exposure to regenerative UV. It is obvious that a high degree of cross-disciplinary collaboration will be significant.

Long-term monitoring of patents and publications on photocatalysis has yielded about 500 references, of which some 300 relate to coating applications. Of these, over 150 employ fluoro and/or silicone resins. Indeed, the subject has assumed such importance that the Paint Research Association has recently published a set of selected abstracts on photocatalysis.

UV and hygienic coatings

Ultraviolet light is central to the future of surface sterilisation. The band known as UVC, generally from 200 to 275nm, provides germicidal activity. The shorter the wavelength, the higher its energy and generally the higher its germicidal effect. Developments in economics, methods of generation and wavelength selectivity are rapidly taking place.

The issues of greatest interest in respect of hygienic systems are:

- germicidal action – low intensity for surface inactivation, high intensity gives lethal effects;
- ozone generation;
- photocatalyst regeneration;
- chemiluminescence analysis;
- activation of cleaning precursors;
- surface preparation;
- air purification in synergism with photocatalysis;
- provision of designer peelable adhesives for dry paint films;
- possible synergism between photocatalytic antibacterial activity and germicidal action of UV itself.

Excimer technologies

Excimer (excited dimer) lasers are being used extensively in narrowband surface processing applications to provide high photon fluxes at specific wavelengths. They have proved much faster than low-pressure mercury lamps in photochemical cleaning of surfaces such as liquid crystal display panels and semiconductor wafers. The lower wavelengths are synergistic, and lamps at 146 and 172nm combined can cleave even the C-F bonds of fluoropolymers.

Pulsed systems give enhanced effects

The lethal mechanism of high-intensity pulsed UV may be different from that of low-intensity UV and, in some circumstances, pulsed UV systems are claimed to be more effective against contaminating micro-organisms than continuous flooding units.[7] With pulses of a few nanoseconds, some modern lasers can deliver the same kind of overall power as conventional types, but the energy is more concentrated in time. However, such systems also have the potential to initiate faster degradation of substrates and coatings.

Innovative coating systems and components

Fluoropolymers

Fluoropolymer-based paints and films may offer ideal properties for the modification of surfaces for contamination resistance and durability. DuPont's polytetrafluoroethylene (PTFE) was the first and the most famous under the 'Teflon' brand. Its widespread use derives from the following properties, all of which contribute to high resistance to biofilm accumulation:

- easy clean;
- non-stick;
- hydrophobic;
- smooth;
- chemically resistant;
- steam-cleanable;
- maximum service temperature 260°C.

A wide range of fluorinated or fluoro-modified coatings are based on novel resin systems from major fluoropolymer producers such as DuPont, Atofina, Asahi Glass, Daikin, 3M and Solvay. Aqueous types are available, as are room temperature curing systems. Polyvinylidene fluoride (PVDF)/acrylic combinations such as Kynar from Atofina and others from Solvay/Ausimont and Kuhrea are accepted as providing supreme weathering and UV resistance for exterior structures. One of the latest developments is a hydrophilic surface modification which allows water to drain off the surface rather than to 'pearl' and thus leave islands of potential staining.

PTFE is theoretically good for marine antifouling coatings because its low surface energy should inhibit the build-up of biofouling. In practice it appears inferior to the higher surface energy silicones. This may be due to the microporosity of PTFE, or to the greater rigidity of the PTFE backbone compared to that of flexible siloxanes. Thus the ideal materials for hygienic coatings may be fluorosilicones, combining silane surface-anchorage, a flexible siloxane linkage and fluoro groups at the air interface to present a resistant finish. A significant cost factor is the ability to engineer a fluoro-rich surface, making economic use of the fluoro resin properties where they are required and enabling the selection of cheaper resins for the bulk.

Spheres of influence

Dendrimers are nearly spherical hyperbranched macromolecules with a well-defined three-dimensional structure. They may have large numbers of reactive end-group functionalities plus shielded interior voids. The molecular weight, size and interior architecture of dendrimers can be controlled with high precision, creating tailored interior cavities or channels with properties differing from the exterior. This allows the protection, transport and delivery of guest molecules both within the surface zone and the encapsulated core.

Organosilicone chemistry, and especially carbosilane chemistry, offers a number of high-yield selective reactions for dendrimer construction. Due to the high number of structural pathways in dendritic systems, carbosilane dendrimers have been envisaged as polymeric supports for multi-site and redox-active systems such as dendrimer bound catalysts.

The ability to combine multiple functions allows for the development of antimicrobial surface activity and/or controlled release from the internal sponge characteristics. Thus it is possible to envisage synergistic combinations of metal ions with antibacterials and perhaps photocatalysts. One company has patented a detergent which incorporated dendrimeric ligands and metallo-complexes as bleach activators.[8]

Prefabricated paint – the use of dry film coatings

'Dry paint films' are another possible approach to hygienic wall coatings. These are single films or laminates applied to a surface without water or solvents and fixed by pressure-sensitive or hot-melt adhesives. With ultrasonic or heat/pressure 'welding' they could be effectively seamless, with overlaps at floor and ceiling. Pipework could be encapsulated by shrink-wrap versions. 'Smart' adhesives not only provide ease of application and tenacity but can also be debonded to yield ease of removal followed by recycling.

Such films can be pigmented, decorated, metal backed, surface-modified, have logos incorporated, and so on. In hygienic applications, the uppermost film could be, for example, a highly resistant fluoro compound with built-in or post-applied biocidal coatings. Dry film coatings are already in use, not only to provide logos on vehicles, but in demanding aerospace applications to decorate complete tailfins and protect nose cones. Imagine the prospects for global food chains, with premises internally decorated with hygienic, durable fluoro films incorporating decorative scenes or logos!

A further extension of film technology could be to apply a durable polymer film and then spray on a strippable coating which could be removed and replaced at regular intervals. An additional refinement could be built-in 'remove me' indicators to signal contamination. There is thus major potential business not only in the supply and application of films but also their maintenance, removal, replenishment and recycling.

Nanotechnology

Matter in the form of minute particles in the nanometre range may exhibit novel properties. Nanoparticles with controlled morphology and functionality may feature as both passive and active coating additives in surface modification for hygienic systems. Though the current focus is on nanoparticles we should not ignore the potential for nanoemulsions, particularly for novel cleaning systems.

Inspection and testing

Crucially, with all this potential for the development of diverse hygienic technologies, we lack standards. How do we tell that a surface is really clean, or identify and measure contamination? Consider the following fairly evident problems:

- A surface that looks clean may be highly contaminated.
- A surface which appears smooth and unbroken to the naked eye may be seriously abraded and full of microcracks.
- If we wipe a surface we may measure the amount of contamination picked up by the wiping material but do we normally measure what has *not* been removed? How can we in fact do so?
- Do we kill micro-organisms but leave the dead behind to act as anchorages and nutrition for the next generation of colonists?
- At what rate does germicidal UV radiation degrade coatings?
- How do we monitor the build-up of contamination in out-of-sight areas in HVAC systems?

If we cannot qualify and quantify bio-contamination, then how can we design for its prevention and measure the success of that action? Even the energy and wavelengths generated by UV systems may change due to contamination, energy input variation and component ageing. It is thus essential to monitor output with radiometers.

Consider, too, that biocidal surfaces are generally tested and approved under conventional laboratory conditions. The Petri dish inoculation of a standard nutrient gel by one type of micro-organism is not the same as the formation of a complex biofilm on a contaminated surface; it cannot be expected to indicate the effectiveness of biocides accurately and probably cannot predict long-term practical service performance. Additionally, the test time is too slow for immediate feedback responses.

The food, drink, health and related industries need faster methods to give assurance of food safety and to monitor critical points. An advanced regime for hygienic surfaces requires efficient and rapid means of detection of biofilm contamination at the earliest stage.

Sensor perceptions

Encouraging developments are taking place in more rapid identification and characterisation which may eventually enable rapid on-site diagnosis and reme-

Table 3: Future developments in hygienic coatings

Design issues	*Innovative technologies*	*R&D areas*
Resin selection	Insoluble contact disinfection	Easy clean surfaces
Formulation	Surface catalysis	Non-migratory biocides
Additives – general	Photocatalytic (regenerable) metal oxides	Refreshable antimicrobial polymers
Additives – active	Amplification of hydrogen peroxide activity	Safer sterilants and cleaning compounds
Resistance	Cleaning precursors	Solid contact biocides
Durability	Antibacterial activated carbons	Metal-based and ionic additives
Application methods	Enzymes	Fluoro-based coatings
Touch-up potential	Nanotechnology	Modified fluoroalkyl siloxanes
Contamination – prevention	Nanoemulsions	Prefabricated paint films
Identification of contamination	Silicone-based quaternary ammonium compounds	Smart adhesives for films
Cleaning systems/regularity	Ultrasound and microwave	Dendrimers
Selection advice	Ozone	Photocatalytic TiO_2 – novel types
Removal	Pulsed and selective UV	UV developments and use
Replacement	Controlled release products	Remote sensing
Recycling	Selected synergism of the above	Detection, analysis and identification

dial action. The development of thin-film and nanotechnology-based biosensors is advancing rapidly but as yet there is still no rapid and convenient on-site 'species identification' method.

Another problem may be overkill with disinfectants and sterilisation, leaving chemical residues on the surfaces. Detection and elimination of these residues is also important. Future possibilities may include self-adhesive bio-indicators/identifiers placed at strategic positions and strippable coatings incorporating detection compounds to indicate growth on the surface. Automatic and remote sensing is also called for, particularly for inaccessible areas such as HVAC systems. Ultimately, there is also an absolute need for internationally accepted definitions, standards and test methods for hygienic coatings and cleaning processes.

Conclusion: Solutions for the future

Modern hygiene requirements cannot be achieved by the use of biocides alone nor by the superficial use of aggressive cleaning agents, because airborne contamination is constantly replenished. Hygienic coating is about the integration of all components and systems with beneficial synergisms. Intelligent initial design, optimum coating selection, efficient monitoring, a regular cleaning regime and supervisory inspection must be combined to defeat ubiquitous, innumerable, mutatable and multifunctional micro-organisms. The message is, that it is not viable to concentrate on just one aspect alone of complex, multifunctional and essential regimes. An intensive and co-ordinated effort by all sectors of the hygienic surface industry with support from the major links in the food and health chains is required to introduce improved systems.

With a trend away from migratory and volatile biocides, the use of regenerable photocatalytic systems and biocidal solid contact polymers and metals must be considered. There may be a potential to employ safer, mild cleaning precursors that convert to more active products at the surface when action is required. It is vital that the cleaning products and mechanical actions do not impede or degrade the 'actives' within the coating. Conversely, it may be feasible to employ cleaning agents which replenish or refresh the activity of selected biocidal additives.

UV and pulsed UV radiation may potentially be used for germicidal purposes, photocatalyst regeneration, ozone generation and enhancing the activity of surface cleaners. But the use of UV radiation is very complicated because its effects on the integrity of the coating and incorporated actives must be considered. Additionally, both UV radiation and ozone are hazardous, so room flooding must be conducted only where secure safety mechanisms can guarantee the absence of all personnel. Improvements in wavelength selection, high-energy systems, and more effective pulsed units, coupled with reflection or 'piping' into difficult areas, suggest that UV irradiation will become an essential aspect of hygienic systems.

Above all, measurement, detection, identification and eradication of contamination must receive attention because what you cannot measure you cannot control. This means not only detection of surface contamination, but also regular monitoring of the coating surface to detect any deterioration such as micro-cracking at the earliest stage.

Many areas of research and development will be involved over the next few years in the development of this industry. The main fields are summarised in Table 3. What sectors of potential R&D are of prime interest to *you*?

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