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Recent Developments in the Technology of Surfactants

Edited by M. R. Porter

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1 Introduction

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The science and use of surface active agents have been utilised by nature and mankind for millennia. Nature has used the science of surface activity in many simple and complex ways, water flowing off a duck's back is an easily observed phenomenon and yet the utilisation of surfactants and surface activity inside the living cell is only now just being appreciated and only very dimly understood.

Surfactants have been used by man for a long time. Soap was used by the Phoenicians and the Romans, and a soap making process was recorded by Plinius in 70 AD. Soap was first made on an industrial scale in the mid-19th century. Sulphonated natural oils were introduced in the latter half of the 19th century, but it was not until the use of petroleum derived fractions in the 1950s that wholly synthetic surfactants were manufactured and used on a large scale. In the Western World (USA, Japan and Europe) wholly synthetic surfactants have overtaken soap as the major volume surfactants and yet in the rest of the world soap remains the dominant surfactant.

The scientific study of surface activity has followed the use of surfactants rather than the use following the theory of surfactants. The practical use of a surfactant has been determined by empirical means, i.e. an organic chemist has produced a surfactant and then it has found its practical end use by a process of trial and error. Using this procedure there is now a considerable volume of knowledge linking chemical structure to end use, but a considerable part of this knowledge is in the form of trade secrets. The prediction of properties and end use, by utilising the theory of surface activity, is still a long way off. It has been stated that we know more of the theory of the sun's activities than that of the theory underlying the washing of clothes.

Over the last 50 years there has been an enormous number of new surfactants produced and many new applications. The field of theoretical surfactant chemistry is now expanding very rapidly after being neglected for many years. The reason for this is due to three quite separate and different features. Firstly, the prospect of diminishing resources of petroleum led to the development, empirically, of enhanced oil recovery by using surfactants. When the oil industry predicted a world shortage of crude oil, millions of dollars/pounds of industrial funds were available for research in the study of emulsification. Considerable progress has now been made since 1970 in this direction.

Secondly, the concern in the Western World on the 'green' issue has led to a far more intense study on the biological effect of synthetic surfactants. This, coupled with methods of analysis which can detect parts per billion of surfactant in the environment, has made the principal users of surfactants, the large detergent companies, spend considerable sums of money in industrial research. This research has been directed at the effects of surfactants on organisms and the fate of the surfactant in the environment, because these are the very questions being asked by the consumers of detergents.

Thirdly, the tremendous growth of study in the biochemical area has now shown the existence of many biological processes to depend upon surface activity, e.g. the penetration of cell walls by invading viruses.

This volume is mainly devoted to looking at the recent developments in surface active technology and the application of surfactants. There is no intention to cover every application, but rather to examine several areas which have not been well covered in recent years. When one examines the theory of surface activity in order to see how far it goes to explain the observed behaviour of surfactants there is one factor above all which quickly becomes apparent. It is that every practical application of surfactants tends to use more than one surfactant and that the surfactants used are very rarely pure homogeneous chemicals and are themselves mixtures. The concept of synergy is very widespread in the use of surfactants. It is very rare to find a practical application where a single pure surfactant performs better than a mixture, often of closely related species. The theory of surface active behaviour is still grappling with this problem. The reason for this problem is not difficult to find and that is most real applications involve more than one surface active property and that they are dynamic systems and not susceptible to most theoretical treatments which are often in the equilibrium state.

A surfactant is often pictured as a simple rod-like hydrophobe with a hydrophilic head. However, many new surfactants are now being produced of more complex structure with more than one hydrophilic head. Such products have been shown to more readily form microemulsions. More complex surfactants with a multitude of hydrophilic groups on a polymeric backbone have long been known, but there are now new families of such products becoming commercially available.

This book has selected areas of the applications of surfactants where synergism and surfactant interactions are commonplace, and one new type of surfactant, the polymeric surfactant. Detergency and enhanced oil recovery must head the list of applications where commercial research has concentrated, but these two subjects are now being covered regularly in reviews and symposia. The book covers four applications: surfactants in agriculture, surfactant–biocide interactions, defoaming and the use of surfactants as corrosion inhibitors, and a description of polymeric surfactants.

Surfactants in agriculture have two main applications. As formulation aids they are used as emulsifiers and dispersing agents in emulsifiable concentrates, suspension concentrates, water dispersible granules and wettable powders. Examples of formulations show the invariable use of mixtures. The other major use is as activity enhancers where the use of the surfactant plus a herbicide can increase the activity of the herbicide so that much lower quantities of active ingredients are released into the environment. The mechanism by which the interaction occurs is by no means understood.

The risk of food poisoning has dramatically increased in the UK in recent years. Keeping working surfaces in the home and manufacturing equipment in the food industry clean and germ free are an essential part in the fight to reduce this risk. The primary weapon is a combination of surfactant which cleans and a biocide which kills germs. In order to find the most effective combination of surfactant/biocide it has been found that interactions do occur with the surfactant affecting the performance of the biocide. Many surfactant–biocide combinations are very effective cleaners and sometimes a synergistic effect is observed whereby the bactericidal efficiency is boosted by the surfactant. On the other hand, it is equally recognised that many surfactant–biocide combinations are antagonistic and result in a much reduced biocidal efficiency. There are so many possible combinations that systematic study proceeds slowly.

Probably, the application area where synergy is shown to its most spectacular effect is in the area of defoamers. Defoamers are generally used at low concentrations, 2% being a high concentration and down to 0·01% being common in the paper industry. The effect of the correct choice of surfactant can give improvements in efficiency of 10 to 100-fold. Such formulated products tend to be kept as trade secrets, the user only being concerned with the performance of the mixture. There are a large number of different foaming problems in industry: the textile industry, the fermentation industry, the food industry, the surface coating industries, pulp and paper manufacture, water treatment, sewage treatment, petroleum processing, the building industry, the chemical industry and pharmaceutical industry all have foam problems of various types. Each industry has found, generally by trial and error, the solution to these foam problems by the correct selection of defoamers or antifoams, all of which depend upon their surface activity as the mechanism of action.

A characteristic property of surfactants is that they are attracted to and adsorbed at the solid/liquid interface. This property has been put to good use by the development of specific surfactants which will adsorb on to the surface of metals and particularly iron. Even at very low concentrations in solution (less than 0·01%) they can perform as effective rust and corrosion inhibitors. By varying the chemical structure of the surfactant a whole series of products with varying water and oil solubility can be made which can then be used in environments ranging from oil through oil/water mixtures to aqueous systems. The exact mechanism by which the surfactant is adsorbed and then interferes with the corrosion mechanism has been the subject of considerable study, but still awaits a conclusive explanation.

The stabilisation of solid particle in nonaqueous media has traditionally been achieved with synthetic resins based on natural fatty acids such as long oil alkyd resins, but the development of increasingly sophisticated inks and paints has led to the requirement of more effective stabilising agents. The new products now being used are described as polymeric surfactants due to the mechanism of using an anchoring group or groups in order to anchor a polymer chain on to a substrate and thereby provide a barrier against coalescence of the particles. The largest use and the widest studied application of such polymeric surfactants is in surface coatings. There are now a wide range of polymeric surfactants commercially available for improving the application of paints and printing inks. Other applications of similar products are oil based drilling fluids, lubricating oil additives, ceramics, magnetic tapes and discs and inverse emulsion polymerisation processes. It is unfortunate that the manufacturers of these products do not reveal the exact composition of these new materials. There are, however, enough published papers and patents which describe the general type of structure and mode of action of the polymeric surfactants.

2 Surfactants in agrochemical formulations

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2.1 Introduction

Surfactant usage in Western Europe, the USA and Japan in the crop protection market is estimated to be in excess of 100 000 tonnes. Surfactants find two major applications in the formulation of agrochemical toxicants. As formulation aids they enable concentrates to be readily formulated and applied by the end user, and as adjuvants they enhance the biological activity and efficacy of specific 'actives'. Both aspects will be considered in detail with particular attention being paid to the move from simple formulations to more complex, multicomponent ones. Present day demands for improved environmental acceptability regarding toxicity and the ultimate fate of residues in the environment and for enhanced performance are prerequisites.

2.1.1 *The active ingredients*

Agrochemical toxicants or 'actives' comprise the following major classes.

2.1.1.1 Herbicides These are ranges of materials developed to selectively kill weeds usually in the presence of specific crops. The best known products are found in the following three classifications:

Organic nitrogen-containing products

Triazines	e.g., atrazine, simazine
Ureas	e.g., diuron, linuron
Carbamates	e.g., propham, chloropham
Amides	e.g., propanil

Phenoxyalkanoic acids
Salts and esters of 2,4-dichlorophenoxyacetic acid (2,4-D)
4-Chloro-2-methylphenoxyacetic acid (MCPA)
Bipyridinium compounds
e.g., Paraquat.

2.1.1.2 Insecticides Insecticides for the control of insects may be sub-divided into three main chemical types:

Organochlorine compounds
e.g. DDT, dieldrin, toxaphene, chlordane, lindane, heptachlor
Organophosphorus compounds
e.g. phosdrin, malathion, diazinon, Parathion-ethyl and -methyl.
Pyrethrum and pyrethroids
e.g., natural pyrethrum extracted from plants and synthetic analogues.

2.1.1.3 Fungicides These comprise an extensive range of chemical species with products such as sulphur, captan (*N*-(trichloromethylthio)-cyclohex-4-ene-1,2-dicarboximide) and folpet (*N*-(trichloromethylthio)-phthalimide) being well known for their fungicidal properties. Other classes of more specialised pesticides include *acaricides* for the control of mites and ticks, e.g. dicofol(2,2,2-trichloro-1,1-di(4-chlorophenyl)ethanol) and *nematocides* for the control of wire worms and cut worms, e.g. ethylene dibromide and dibromochloropropane (DBCP), these materials being applied as soil fumigants. A comprehensive description of these and many other agrochemical species are to be found in the literature.[1–3]

2.1.2 *Agrochemical formulations*

The successful employment of any active agrochemical depends on its correct formulation into a preparation that can be applied for crop protection, with safety to those applying the material, to animal life and to the crop in question.

The earliest pesticide formulations were dusts, wettable powders, aqueous solutions and even some casein-stabilised mineral oil-in-water emulsions for orchard spray applications. Today, there are three general methods of applying agrochemical actives:

—Spraying with water or oils as the principal carriers
—Dusting with a fine dry powder carrier
—Fumigation where the toxicant is applied as a gas.

By far the most important method of application is spraying, and here surfactants are employed to produce a variety of 'concentrates' in water, oil or powder/granular form. These concentrates have to be readily dilutable and maintain sufficient stability on dilution to be readily applied without problems of separation.

The advent of synthetic surface active agents has enabled a whole range of formulation classes to be developed. These may be summarised as follows.

2.1.2.1 Emulsifiable concentrates (ECs) The active ingredient is dissolved in a solvent which is commonly xylene, solvent naphtha, odourless kerosene or other proprietary hydrocarbon solvent. Surfactant emulsifiers are formulated into these systems to ensure spontaneous and stable emulsification. Careful selection of a 'balanced pair' emulsifier blend is frequently necessary to ensure emulsion dilution stability is maintained over widely differing climatic conditions and degrees of water hardness.

Emulsifier blends have to be tailored to the active agrochemical in question. However, the principal emulsifier, which is extensively used in many EC formulations, is the calcium salt of a linear or branched chain dodecylbenzenesulphonate, generally available as a 70% active solution in butanol. Coemulsifiers commonly formulated with this material to produce a 'balanced pair' are often nonionic in character and include castor oil ethoxylates (frequently the 40 mole ethoxylate), nonylphenol ethoxylates and ethylene oxide–propylene oxide block copolymers. In particular, the more hydrophilic coemulsifiers improve stability against coalescence of the dilute emulsions formed from the concentrate. Typical *emulsifiable concentrate* formulations are given below:

(*i*) *Bromophos*

Bromophos	50·0% (w/v)
Calcium dodecylbenzenesulphonate	2·5%
Castor oil ethoxylate (40 moles EO)	2·5%
Hydrocarbon solvent (predominantly aromatic)	to 100 vols

Bromophos is a nonsystemic contact and stomach insecticide and is 2,5-dichlorophenyl *O,O*-dimethyl phosphorothioate.

(*ii*) *Malathion* (*technical grade*)

Malathion	50·4% (w/v)
Calcium dodecylbenzenesulphonate	4·5%
Castor oil ethoxylate (40 moles EO)	2·8%
Ethylene oxide–propylene oxide copolymer (mol. wt 2500/30% EO)	3·0%
Xylene	to 100 vols

Malathion is a nonsystemic insecticide and acaricide of low mammalian toxicity and is diethyl (dimethoxythiophosphorylthio)succinate.

(*iii*) *2,4-D isooctyl ester*

2,4-D isooctyl ester	93·0% (w/w)
Isopropylamine salt of a dodecylbenzenesulphonic acid	4·2%
Nonylphenol ethoxylate (8 EO)	2·8%

This is an example of a 'solvent-free' EC. 2-4-D isooctyl ester is a member of the range of salts and esters of (2-4-dichlorophenoxy)acetic acid. They are all systemic herbicides, widely used for weed control in cereals and other crops.

(*iv*) *Permethrin*

Permethrin	25·0% (w/v)
Calcium dodecylbenzenesulphonate	1.3%
Nonylphenol ethoxylate (14 EO)	3·5%
Alkylphenol ethoxylate –formaldehyde condensate	1·2%
Aromatic hydrocarbon solvent	to 100 vols

Permethrin is a contact insecticide effective against a broad range of pests and is chemically, 3-phenoxybenzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate.

EC formulations are both easy to prepare and to apply. However, they have two distinct disadvantages: flammability and problems of phytotoxicity. Nevertheless, they remain the largest single formulation class used in crop protection today. Health, safety and environmental pressures on selected solvents have begun to influence the development of both safer ECs and other classes of formulation.

2.1.2.2 Flowables/suspension concentrates Aqueous flowables or suspension concentrates consist of an insoluble toxicant in a concentrated aqueous suspension. Such formulations must possess very good storage stability, which encompasses no precipitation on storage, good hydrolytic stability of the toxicant and excellent viscosity stability between −20° and +50°C. The highest possible toxicant concentration should be achieved and the suspension concentrate viscosity should be low enough to ensure ease of handling and subsequent dispersibility.

Flowables may be manufactured by dissolving dispersants and wetting agents in a cosolvent, e.g. ethylene glycol, followed by addition of the agrochemical active and water. Blending is achieved using a high speed mixer followed by milling of the dispersion down to about 4 μm. In both the mixing and milling stages it may be necessary to incorporate an antifoaming agent. The milled dispersion is then allowed to degas, sometimes with the aid of an applied vacuum.

Flowables, which have the advantage of high toxicant concentration, are easy to disperse and apply and are free of the flammability problems associated with emulsifiable concentrates.

An increasing number of active ingredients lend themselves to be formulated as suspension concentrates, and a balanced combination of wetting agents, dispersants, viscosity modifiers and antifreeze compounds is vital, if a stable formulation with prolonged shelf life is to be achieved. Flowables are *less* prone to exhibit phytotoxic side-effects.

Typical *flowable* formulations are as follows:

(*i*) *Folpet*

Folpet	50·0% (w/v)
Sodium dioctyl sulphosuccinate	1·0%
Castor oil ethoxylate (40 EO)	2·5%
Ethylene oxide–propylene oxide copolymer (mol. wt 5000, 50% EO)	1·5%
Ethylene glycol	5·5%
Xanthan gum	0·1%
Silicone defoamer	0·1%
Water	to 100 vols

Folpet is *N*-(trichloromethylthio)phthalimide, a protectant fungicide.

(*ii*) *Copper oxychloride*

Copper oxychloride	60·0% (w/v)
Isodecanol ether phosphate, triethanolamine salt	1·75%
Ethylene oxide–propylene oxide block co-polymer (mol. wt 5000, 50% EO)	1·25%
Ethylene glycol	6·0%
Silicone defoamer	0·1%
Xanthan gum	0·1%
Water	to 100 vols

Copper oxychloride, $ClCu_2H_3O_3$, is a protectant fungicide used to control fungi on potatoes and hops.

(*iii*) *Sulphur*

Sulphur	70·0–80·0% (w/v)
Tristyryl ether phosphate, triethanolamine salt	4·0%
Potassium salt of oleic acid sulphonate	1·5%
Ethylene glycol	6·0%
Silicone defoamer	0·1%
Xanthan gum	0·1%
Water	to 100 vols

Sulphur is a well known fungicide, which is still frequently used in powder form.

(*iv*) *Atrazine/Aminotriazole mixed flowable*

Atrazine	40·0% (w/v)
Aminotriazole	10·0%
Isodecanol ether phosphate, triethanolamine salt	3·0%
Silicone defoamer	0·05%
Xanthan gum	0·2%
Water	to 100 vols

Atrazine is 6-chloro-*N*-ethyl-*N'*-isopropyl-1,3,5-triazinediyl-2,4-diamine and is a selective pre- and post-emergence herbicide. Aminotriazole, 1*H*-1,2,4-triazol-3-ylamine, is a nonselective herbicide absorbed by roots and leaves and translocated.

2.1.2.3 Water dispersible granules Water dispersible granules (WDGs), sometimes referred to as 'dry flowables' are granular compositions exhibiting rapid 'break-up' in the mix tank to produce a stable dispersion or emulsion. The granules themselves must not 'cake' on storage. Generally WDGs contain toxicant, one or more wetters and dispersants, some water and an inert filler. Water dispersible granules can be manufactured by premixing the agrochemical active(s), filler and dispersants in a pan granulator and then spraying water on to the mixed powder with a monitored dosage of wetting agents. Once the granules are formed, they may be transferred to a bed drier to remove the water.

Again, this formulation class has the advantage of achieving high concentrations of toxicant. The products are easy to apply and are dust free. On the other hand, until recently, expensive production plant has been required.

Again with the cost and environmental restrictions on petroleum solvents in pesticide formulations, 'dry flowables' offer an alternative approach for the formulator. Manufacturing techniques now include spray drying, fluidised bed, pan granulation and extrusion. In all cases, drying must be carefully controlled to avoid thermal degradation of the 'active'. Typical WDG formulations are as follows:

(*i*) *Atrazine*

Atrazine	85·0% (w/w)
C_{10} fatty alcohol + 7 EO	4·0%
Sodium salt of naphthalene sulphonic acid–formaldehyde condensate	5·0%
Binder	0·5%
Diluent	5·5%

Atrazine is used as a selective pre- and post-emergence herbicide.

(*ii*) *Captan*

Captan	91·0% (w/w)
Nonylphenol ethoxylate–formaldehyde condensate	3·0%
Ammonium salt of nonylphenol ether (4 EO) sulphate	2·5%
Sodium salt of naphthalene sulphonic acid–formaldehyde condensate	3·0%
Binder	0·5%

Captan is a fungicide used to control diseases in many fruit and vegetable crops. It is also used to protect young plants by spraying or root dip to prevent rot or damping-off.

2.1.2.4 Wettable powders Wettable powders consist of an active ingredient absorbed on to one or more inert fillers, such as kaolin, chalk or thermal silica, plus wetting agents, one or more dispersants and optional additives such as anticaking, antistatic and antifoaming agents. Wettable powders must exhibit easy wetting, rapid and complete dispersibility, good suspension stability and low foam, and must not 'cake' on storage. They have the advantage of being very cheap formulations, but suffer from a number of disadvantages including low concentrations of active ingredient and handling difficulties, particularly dusting problems. Typical formulations for wettable powders would be as follows:

(*i*) *Diuron*

Diuron	80·0% (w/w)
Sodium salt of diisopropyl naphthalenesulphonate	1·5%
Sodium salt of naphthalenesulphonic acid formaldehyde condensate	2·5%
Kaolin	16·0%

Diuron is a substituted urea compound used as a pre- and post-emergence herbicide. Chemically it is 3-(3,4-dichlorophenyl)-1,1-dimethylurea, see Fig. 2.1.

(*ii*) *Carbendazim*

Carbendazim	50·0% (w/w)
Sodium dodecylbenzenesulphonate	3·5%
Sodium salt of naphthalenesulphonic acid formaldehyde condensate	4·0%
Kaolin	42·5%

Carbendazim is the benzylimidazole fungicide, 2-(methoxycarbonylamino)benzimidazole, see Fig. 2.2.

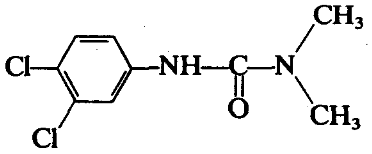

Fig. 2.1 Diuron.

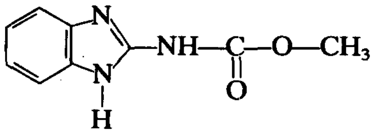

Fig. 2.2 Carbendazim.

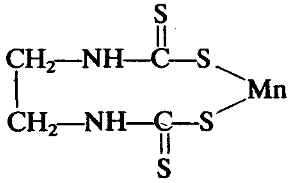

Fig. 2.3 Maneb.

(*iii*) *Maneb*

Maneb	80·0% (w/w)
Sodium dodecylbenzenesulphonate	2·5%
Sodium salt of naphthalenesulphonic acid–formaldehyde condensate	1·5%
Kaolin	16·0%

Maneb is a carbamate fungicide and is chemically manganous ethylene bisdithiocarbamate, see Fig. 2.3.

2.2 Future trends in agrochemical formulations

Future trends in agrochemical formulations will be governed by many factors. These will include the development of more cost-effective production methods for certain types of formulation, environmental pressures to use less or even eliminate the use of particular solvents, the banning of some environmentally unacceptable toxicants, pressure to reduce the dosage per hectare and, as new 'actives' become more difficult to develop and more costly to register, blends of two or more components will be considered. Increased interest in additives, which give a synergistic increase in performance, and methods of controlling the release of actives will likewise gain importance.

ECs will continue to be the dominant class of formulation for many years hence, with a gradual increase in the development of flowable systems. However, the following areas are seen to be of particular interest regarding future developments in agrochemical formulation technology and will be considered in more detail in subsequent sections of this chapter:

—Water dispersible granules (WDGs)
—Microemulsions
—Formulation of two or more active ingredients
—Activity enhancers
—Microencapsulation for controlled release
—Miscellaneous surfactant applications

It is difficult to predict the long-term growth potential for surfactants in the agrochemical industry as opposing factors can influence the growth or decline of this market. There is no doubt that, with increased world population, the need for effective crop protection in the future will continue to be a major factor in the food chain. Although a more judicious use of pesticides and herbicides will undoubtedly be necessary to protect the environment while no viable large-scale alternatives currently exist. In the USA and Western Europe reduced farm acreage and increasing environmental concern are having a dramatic effect on the herbicides market.[4] Weedkillers account for more than 40% of the total agrochemicals market, but within this sector there is a shift to more active and selective compounds.

Global sales of all agrochemicals slipped by about 1% in 1987 to about $20 billion.[5–7] Environmental pressures are leading to the development of selective herbicides, which require less active ingredient and are targeted at new sites of metabolic action within plants.

One example is the range of herbicides which inhibit amino acid biosynthesis. DuPont has developed the sulphurylurea class of herbicides that block the production of the key branched chain amino acids valine and isoleucine. Sulphurylurea herbicides block the synthesis of these amino acids by knocking out the enzyme acetolactate synthase, which catalyses the first step in the pathway for biosynthesis. An additional advantage claimed by DuPont is that acetolactate synthase is a rare enzyme, so less active ingredient is required to inhibit the enzyme. It is of course important that the herbicide does not harm the crop in question. It has been demonstrated that chlorosulphuron (1-(2-chlorophenylsulphonyl)-3-(4-methoxy-6-methyl)-1,3-5-triazin-2-yl)urea is broken down by cereal crops, and the cereal has been found to contain a key enzyme which is not affected by the herbicide.

Hence, the introduction of a herbicide-resistant enzyme gene into a commercially important crop offers intriguing possibilities. Consequently, the role of the plant biotechnologist, which couples both genetic engineering and plant cell culture, offers a promising strategy. Some plants which have already been developed using plant breeding techniques are resistant to important herbicides such as the triazines. Companies are now trying to accelerate this process by transferring genetic blueprints of resistance into crops directly.

Hence, the long-term usage of surfactants as formulation aids and adjuvants could be in question, particularly in major crop areas where resistance is 'built-in'. Nevertheless, in the forthcoming decade, the following formulation classes and formulation aids will gain in importance.

2.2.1 *Water dispersible granules (WDGs)*

A high growth rate in WDGs has been predicted,[8] mainly due to improved plant processes. Advantages of WDGs over wettable powder and flowables include uniform particle size, dust free, nonsplashing products which are easy to deal with when there is a spillage. They have no long-term stability problems and protection against frost is unnecessary.

Five processes now operate for WDG production. These are

1. Extrusion.
2. Pan granulation.
3. Spray drying.
4. Fluid-bed granulation.
5. Mixing agglomeration.

The advantages and disadvantages of each process are given in the table from Seaman's paper on trends in pesticide formulations[8] (see Table 2.1).

In most cases, formulations contain a very hydrophilic dispersant, and products such as naphthalenesulphonate formaldehyde condensates, which are used in wettable powders, are also suitable for WDG production. Other additives such as wetting agents (alkyl or dialkyl

Table 2.1 Comparison of granulation processes

Extrusion	Multistage operation	Dusty operation	Suitable for heat sensitive materials	Optional size of plant	Produces hard compact granules with some dust
Pan granulation	Multistage operation	Dusty operation	Suitable for heat sensitive materials	Optional size of plant	Produces wide size range with some dust, needs sieving
Spray drying	Single-stage operation	Enclosed operation	Not suitable for heat sensitive materials	Requires large plant	Fine product
Fluid-bed granulation	Single-stage operation small amount of recycle	Enclosed operation	Suitable for materials with m.p. >80°C	Optional size of plant	Produces fairly uniform grains, optional size, essentially dust free
Mixing agglomeration	Multistage operation	Partly enclosed operation	Suitable for heat sensitive materials	Optional size of plant	Produces wide size range, irregular shaped grains, need sieving

naphthalenesulphonates, dioctyl sulphosuccinate, etc) and disintegrating aids may also be employed. Bentonite clays are commonly used as disintegrating aids as they are highly water soluble and absorbent. Polyvinyl pyrrolidone may also be used as a binding agent.

Problems which remain in the area of WDGs include higher product and capital costs, problems of incorporation of liquid active ingredients and wetting agents, recycling of off-size materials, more stringent control of toxic dusts and difficulty in maintaining the particle size of actives at micrometre level. Nevertheless, there is no doubt that WDGs will grow in importance as a formulation class. As less capital intensive, more flexible processes evolve, ideally ones avoiding recycling and drying, so WDGs will increase in importance. The demand will develop for products containing more than one active ingredient or processes allowing incorporation of liquids and low melt solids.

Recent literature reveals the use of a broad range of wetters and dispersants, including poly(styryl)phenol ethers[9] and their phosphate ester derivatives,[10] naphthalenesulphonates,[11,12] polycarboxylates based on acrylic acid and its copolymers with itaconic acid, and styrene–maleic acid and diisobutylene maleic acid copolymers.[13,14] Other papers and patents of recent interest are also cited.[15–23]

2.2.2 *Microemulsions*

Microemulsions are thermodynamically stable, transparent emulsions, stable over a wide temperature range and of very fine droplet size (below 0·1 μm)[24–26] and recently such concentrated aqueous emulsions of insecticides have been introduced as an alternative to the solvent-containing emulsifiable concentrates. The stability of microemulsions is attributed to the presence of near-zero interfacial tensions at equilibrium and also a minimum or potentially negative Gibbs free energy. Several surfactants are required to achieve low interfacial tensions. When one of the surfactants exhibits solubility in the water phase and the other is soluble in the organic phase, they have only a marginal effect on each other and sometimes their combined effect is large enough to reduce the interfacial tension to almost zero at finite concentrations. However, although detailed microemulsion theory is found throughout recent literature, the practical production of microemulsions remains to some degree an art.

To ensure the desired stability, in addition to the use of surfactants, microemulsions frequently contain adjuvants such as antifoaming agents, antifreezing agents, thickeners and antimicrobial preservatives. Microemulsion may be produced as a concentrate for use as is or may be further diluted.

Surfactants with large hydrophobes such as polyaryl phenol ethoxylates and their sulphated derivatives feature amongst the more successful coemulsifiers for microemulsion production.[27] For example, insecticidal microemulsion formulations for a variety of active concentrations of a synthetic pyrethroid from 1·33 to 20·0% are shown in Table 2.2.

Silicone antifoaming agents are frequently used to prevent foam formation and air entrainment during manufacture. Likewise antifreezing agents such as ethylene glycol or diethylene glycol at levels up to 10% are added to ensure greater microemulsion stability.

Thickening agents such as cellulose derivatives (and required preservatives), polyacrylamides, natural gums, polyvinyl alcohols or pyrrolidones may also be added to the microemulsion to further enhance stability.

Further work on microemulsions recently reported in the literature is summarised in the reference section.[28–31] Due to the higher costs of manufacture and high levels of specialised emulsifier, the future growth of microemulsions may be limited to expensive active ingredients such as pyrethroids and organophosphorus compounds.

Table 2.2 Microemulsions of a synthetic pyrethroid

Synthetic pyrethroid (%, w/v)	*Surfactant (%, w/v)*			*Antifreeze (%, w/v)*	*Antifoam (%, w/v)*	*Other additives (%, w/v)*
	A	*B*	*C*			
1·33	1·33	0·89	0·53	2·0	0·05	—
2·5	—	3·0	2·0	2·0	0·05	0·38 polyacrylamide
4·0	3·75	2·67	1·6	2·0	0·05	0·38 polyacrylamide
10·0	7·0	5·0	3·0	5·0	0·075	—
20·0	—	15·0	10·0	—	—	—

A: Ammonium salt of sulphated distyryl phenol ethoxylate (5 EO).
B: Tristyryl phenol ethoxylate (17 EO).
C: 70% alcoholic solution of calcium dodecylbenzenesulphonate.

Actives also have to be hydrolytically stable. Nevertheless, their long-term stability, ease of dilution, lack of solvent and ability to contain up to 60% of active ingredient make them an attractive alternative to some other formulations.

2.2.3 *Mixtures of agrochemical active ingredients*

There is increasing difficulty in the discovery of new agrochemical actives and subsequent problems of product approval and registration in Europe or the USA, It is estimated that one agrochemical active ingredient was commercialised for every 1800 compounds screened in 1956, whereas the figure was 7000 in 1970 and 12 000 in 1977. To avoid the high cost of research and approvals, composite or even synergist effects are being sought by the use of two or more active constituents. Hence, the interest in combinations of toxicants and the resulting greater formulation demand on the surfactants employed in these systems.

The situation is further exacerbated by the barring of certain well-established toxicants, pressure on reformulation to less hazardous cosolvents and increased demand for compliance with the USA's EPA (Environmental Protection Agency) Regulations and other regulatory requirements, e.g. the UK's Pesticide Safety Precautions Scheme (PSPS). Mixed formulations, commonly a blend of herbicides, are also gaining in popularity because of their convenience, which enables the formulator to apply more readily the correct amount of each component. However, the main problem for the formulator results from the fact that many agrochemical actives are not readily compatible, e.g. a mixture of liquid and insoluble solid actives. There are several potential combinations (Table 2.3) and Seaman in his recent paper[8] provides an excellent summary.

In addition to the pesticides or herbicides, other ingredients such as emulsifiers, crystal growth inhibitors, antisetting agents, dispersants and surfactants, to enhance activity, may be incorporated. These complex mixtures necessitate lengthy screening and storage stability trials due to the complex demands placed on the stabiliser system. A formulation at its simplest could be a mixed flowable, but is more likely to be a combination of formulation types, e.g. a solid and a liquid dispersed in a liquid phase, which could contain solubilised ingredients.

Table 2.3 Combination of actives

Number of components	*Type*	*Formulation possible*
2	Insoluble solid/water insoluble liquid	Emulsifiable concentrate or miscible liquid in ketonic solvent, suspension in EC, suspension emulsion mixture
2	Insoluble solid/water soluble liquid	Suspension in aqueous solution, solid solubilised in aqueous solution
2	Water insoluble liquid/water soluble liquid	Emulsion in aqueous solution, suspension in EC, liquid solubilised in aqueous solution
3	Insoluble solid/water, insoluble liquid/water, soluble solid	Suspension/emulsion/solution, suspension in EC

Many surfactant species find application in these formulations. Polymeric or perhaps more accurately 'oligomeric' surfactants find application in both aqueous and nonaqueous media. In aqueous media these materials consist of a hydrophobic chain or backbone with pendant hydrophilic groups such as polyoxyethylene chains. In nonaqueous systems, oligomeric species, with ionic groups along the backbone and pendant hydrophobic alkyl chains, can be employed. Other polymeric species include various propylene oxide–ethylene oxide block copolymers and naphthalenesulphonate–formaldehyde condensates.

Fatty alcohol and other conventional ethoxylates as well as fatty alcohol ether sulphates and phosphates, and long-chain sorbitan esters and their ethoxylates (polysorbates) have all been used. Of particular interest is the use of anionic and nonionic materials containing a sterically large hydrophobic group. These include the well-known di-/tri-styrylphenol ethoxylates and phosphate ester derivatives used in the emulsifiable concentrate and flowable areas and the lignosulphonates and hydrophobically modified derivatives.

Clearly materials which act as both emulsifiers and dispersants for a wide range of liquid and solid phases will find broad usage in mixed active formulations.

2.2.4 *Agrochemical adjuvants*

Agrochemical adjuvants or activity optimisers are materials which enhance the activity of the active ingredient, usually a herbicide. This can involve obtaining a lower application dosage per hectare in the presence of an adjuvant, broadening the spectrum of activity of the herbicide by killing a broader range of weeds or by increasing the reliability of the formulation so it is more effective over a range of climatic conditions. Adjuvant research is not a new field, the earliest citation documented being dated 1900. However, ecological and economic concerns relating to pesticide usage coupled with a growing interest in new technology are now of increasing interest to scientists in agrochemical research, so that both cost and environmental hazards can be minimised.

Paraquat was an early example of how biological activity could be enhanced by the use of a surfactant. The choice of surfactant was quite specific and it was shown that nonylphenol with 8 moles of ethylene oxide was superior to nonylphenol with 13 moles of ethylene oxide. The nonylphenol + 8 EO nonionic was solubilised in the paraquat with a fatty amine ethoxylate which also acted as an adjuvant. Studies based on radiolabelled paraquat showed that the surfactant adjuvant blend increased herbicide uptake into the weed.

Optimum biological activity and selectivity is an important factor which influences the choice of today's formulations. However, we are only now seeing closer cooperation between surfactant producers, agrochemical toxicant manufacturers and formulators, and agrochemical research stations and academic institutions with expertise in botany.

It is still unclear how a surfactant operates and it is likely to be a combination of various effects. These will include the adhesion of the spray droplet to the leaf surface. One important consideration here can be improvement in 'rain-fastness'. Once the spray droplet is on the leaf surface, the spreading wetting and drying of the droplet become important. For example, penetration of the leaf surface may not be possible and uptake may only be possible through the leaf joint–stem junction. Alternatively, emulsification of the waxy layer covering some leaves may be an initial step, followed by wetting of the leaf surface to allow penetration and uptake through the leaf cuticle.

No clear correlations have emerged between surfactant type and biological activity. Selection still relies on extensive greenhouse and field testing with a representative range of surface active agents. Perhaps the only broad generalisation which can be made is that there are many cases where combinations of a hydrophobic surfactant, which is a good oil or wax emulsifier, and a hydrophilic species, which affords excellent wetting characteristics, act in combination as effective adjuvants.

Fortunately, scientists from the various disciplines are beginning to work together more closely. The need for closer cooperation was illustrated at The First International Symposium on 'Adjuvants for Agrochemicals'. The bibliography supplied at this meeting provides an excellent review of all English language papers (*ca.* 900 references) available on this subject up to mid-1986.[32]

The activity of foliage-applied herbicides will depend on the concentration of active ingredient which reaches the biochemical sites of action. This, in turn, may depend on the efficiency of cuticle retention, cuticle penetration, leaf absorption, translocation and metabolism. Herbicide selectivity is probably due to such differences in these factors between the weed and the crop to be protected. Kirkwood *et al.*,[33] for example, have attempted to study the mode of action and basis of selectivity of isoproturon (*N'*-(4-isopropylphenyl)-*N*,*N*-dimethylurea) applied to wheat, wild oat and black grass without added adjuvant. The chemistry and visual characteristics of the epicuticular waxes of the leaf blade of the test species were studied. All three species contained the same major components as cabbage wax, namely long-chain primary fatty alcohol—C_{23} alcohol in wheat and a C_{26} alcohol in both wild oat and blackgrass, a homologous series of esters and small quantities of variable chain length alkanes. Wax composition was unaffected by leaf age (3–12 weeks) or temperature conditions (15°–25°C). In all three species, the waxes appeared as densely packed rod-like structures. Wax density decreased towards the base of the trichomes. It was noted that pretreatment of the leaves with a surfactant–ethoxylated sorbitan monolaurate (Polysorbate 20) resulted in removal of these rod-like structures.

Absorption, translocation and metabolism characteristics were studied using [^{14}C]-isoproturon, but no correlation between uptake, translocation and selectivity was found. In all species, treatment with a combination of sorbitan monolaurate and ethoxylated sorbitan monolaurate, ranging from HLB 5 to 17, afforded reduced wax retention with low HLB blends, facilitating absorption into the leaf.

The primary site of action for phenylurea herbicides lies in the chloroplast.[34] Further studies indicated that photosynthesis is a primary site of action of foliage-applied isoproturon and that selectivity between wheat, wild oats and blackgrass may be due in part to differential binding of the herbicide to the chloroplast membrane. Differences in metabolism rather than uptake and translocation appear also to be involved. This example illustrates the complexity of the problem in both obtaining an understanding of the mechanisms involved and the practical selection of adjuvant systems.

Fundamental studies in plant tissues have been undertaken. Stolzenberg[35] studied [^{14}C]-labelled octylphenol ethoxylates and found that, in barley, ethoxylated alkylphenols undergo metabolic conversions similar to those of many other xenobiotics in plant tissues. Carbon chain degradation was not observed and there was limited C—O—C bond cleavage. Further recent studies by Stevens and Bukovac[36,37] on octylphenol ethoxylates have made a positive contribution to our knowledge of their mode of action, but, clearly, much more has to be done before an accurate prediction of surfactant performance can be achieved for a specific crop/weed system. The work of the UK Weed Research Division of the University of Bristol's Long Ashton Research Station and its predecessors has contributed greatly to a greater understanding of surfactant action and selectively,[38–44] including the early work on the applications of tallow amine ethoxylates as enhancers for *N*-(phosphonomethyl)glycine (glyphosate).[45]

More recent papers relating to surfactant activity enhancers are given in the reference section of this chapter.[46–69]

2.2.5 *Microencapsulation for controlled release*

A further means of enhancing activity is by way of microencapsulation of various toxicant species. The first microencapsulated pesticide was parathion and was marketed nearly 20 years ago. The parathion was encapsulated by an interfacial process in order to reduce the toxicity of the material with respect to mammals, to increase its persistence and to reduce phytotoxicity, leaching and volatility. It also enabled solvent and emulsifier use to be reduced and a water-based formulation to be produced.

The application of controlled release technology has been slow to reach commercialisation, but a number of active ingredients have

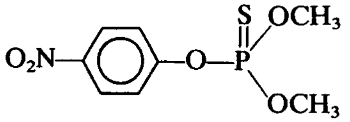

Fig. 2.4 Parathion-methyl.

been encapsulated using interfacial polymerisation as a favoured route as this produces small particle size (10–30 μm) readily formulatable into an aqueous slurry. Many polymer types are used as encapsulating agents including polyesters, polyurethanes and polyureas. The microencapsules generally contain 10–15% of polymer. Some polymeric encapsulants are produced using surfactants by an emulsion polymer route with encapsulation occurring *in situ*.

Release of active is governed by crosslinking of the polymer which governs porosity, wall thickness and the particle size of the microencapsules. The technique is limited to actives insoluble in water, actives which are liquid or soluble in hydrophobic solvents and those which are chemically inert to encapsulating intermediates such as acid chlorides and isocyanates. 'Fulkil' (microencapsulated parathion-methyl) is an organophosphorus insecticide used in vineyards. The parathion-methyl (see Fig. 2.4) is encapsulated in a blend of polyamide and polyurea, and the microcapsules formulation with suitable surfactants into a 240 g/l flowable.

Similarly, 'Capsolane' (microencapsulated ethyl di-propylthiocarbamate (EPTC)) (see Fig. 2.5), a corn herbicide, is encapsulated in a polyurea and formulated into a 350 g/l aqueous flowable.

The benefits of microencapsulation may be demonstrated graphically as shown in Fig. 2.6.

Polyureas have been used to encapsulate pyrethrins and pyrethroids, and hydrophilic surfactants have been incorporated to lower dermal toxicity.[70] The manufacture of polyureas and other encapsulates are the subject of recent patents, some of which employ anionic dispersants and/or fatty alcohol and fatty amine ethoxylates in the process.[71–77]

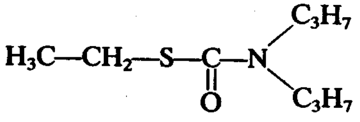

Fig. 2.5 Capsolane.

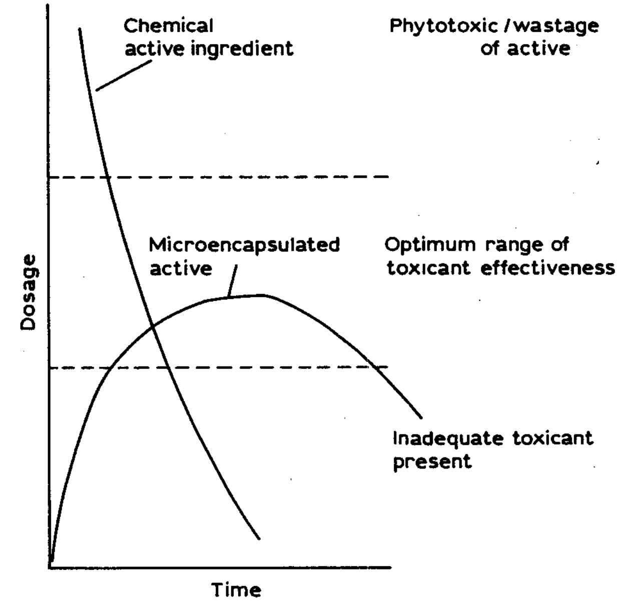

Fig. 2.6 Microencapsulation.

More recently, acrylic and styrene–acrylic polymers containing surfactants have been employed for sustained release formulations of Imidan insecticide.[78] Another example is the successful commercialisation in Australia of 'SusCon Blue', a thermoplastic matrix granule containing chloropyrifos insecticide and unspecified release rate modifiers for the control of several white grub pests found in sugar cane.[79]

2.2.6 *Miscellaneous surfactant applications*

Apart from the classes of agrochemical formulations which have been presented, other applications for surfactants have been cited in recent literature, although it is not always possible to predict the importance of such inventions. These include:

2.2.6.1 Soil additives Surfactant wetting agents have been evaluated as soil additives to improve crop yield and nutrient availability in crops such as corn, potato and soya bean.[80]

Similar work on several materials including surfactants has been undertaken in the study of various phosphorus[81] and carbamoyl group[82] containing pesticides, with positive effect.

2.2.6.2 Plant cryoprotection The protection of crops from frost by the application of surfactant foams has been known for several years,[83] but more recent activity on the use of ethylene oxide–propylene oxide block copolymers as plant cryoprotectants has been noted.[84]

2.2.6.3 Plant growth regulators (PGRs) Today, the use of fertilisers and pesticides has been optimised and is unlikely to afford further improvements in crop yield. The next major improvement in crop yield is likely to come from the increased application of chemical technology to manipulating plant development.[85] The potential for manipulation of crop growth was first realised in the 1930s when it was observed that pineapples could be induced to flower by exposure to ethylene or acetylene. Since that time, the concept of PGRs has moved from one of curiosity to a field of active research, where enhancement in the yield of major arable crops such as cereals, soya beans, sugar beet and cotton has already been achieved by their use. The market for plant growth regulators will grow from $200 million in 1975 to an estimated $900 million by 1990.[86] Many naturally occurring, as well as synthetic, chemicals have been found to be valuable in the control of plant growth, and a range of surfactants has been shown to act as growth stimulators when formulated with them.[87–93] Again, this appears to be a highly selective process with no apparent correlation between surfactant species and its interaction with the PGR. Clearly this will continue to be an area where development will be intensified in coming years.

2.2.6.4 Compatibility agents When agrochemical active ingredients are required to be sprayed in combination with liquid fertilisers it is necessary to use additives to retain stable emulsions or dispersions in the spray tank. Phosphate ester derived wetting and dispersing agents and hydrotropes are particularly recommended to reduce compatibility problems.

2.3 Conclusions

The above examples illustrate the continued and developing usage of surfactants in agrochemical formulations. Environmental pressures to reduce pesticide and herbicide dosage rates and eliminate hazardous solvents, coupled with economic factors, will continue to enhance the development of flowable systems, microemulsions, WDGs and multi-active component blends.

Activity enhancement, controlled release and the modification of PGRs will be important areas where surfactants will play an increasingly more important role in the future. Longer term, much will depend on the successful engineering of crops with resistance to a potential broad variety of insects[94,95] and likewise herbicide-resistant crops where weeds have developed multiple resistance to those herbicides.[96] New crop varieties are being created by plant biotechnologists in order to circumvent the environmental problem of spraying chemicals. Nevertheless, according to a recent report,[97] agrochemical toxicant production will still meet the major requirements of the agricultural industry until well into the 21st century. The EEC market for pesticides was $4530 million in 1987 and is expected to grow to $4770 million (in 1987 dollars) by 1990.

Hence, the requirement for effective emulsifiers, wetting agents, dispersants, surfactant adjuvants, etc. should continue to provide an area of potential growth for the speciality surfactant producer over the forthcoming decades.

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3 Polymeric surfactants

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3.1 Introduction

Polymeric materials, especially high molecular weight ones, have been used to give colloidal stability since almost the dawn of civilisation. In particular, naturally occurring polymeric materials such as egg white, gum arabic and animal glues have been used to make water-based inks and paints pigmented with, e.g. carbon black or metal oxide pigments.

In early 20th century colloid science terminology, this was referred to as 'protection', implying that the dispersion is protected from flocculation or coagulation by an adsorbed layer of the polymeric material. However, in aqueous dispersions the better understood process known as electrostatic stabilisation was probably the most common source of colloidal stability, especially for dispersions of inorganic particles.

In nonaqueous media the situation is rather different in that the relatively low dielectric constant of the medium leads to compression of the electrical double layer and dominance of the Van der Waals attractive forces between particles. In such circumstances the 'protective' action of an adsorbed layer of oligomeric or polymeric molecules offers the only route to colloidal stability. Traditionally this was achieved with, e.g. synthetic resins based on natural fatty acids such as long oil alkyd resins, rosin (abietic acid) and rosin esters, and natural oils such as glycerides of fatty acids. However, the development of increasingly sophisticated inks and paints led to a requirement for more effective surface active agents. Also the use of novel surface coatings as in magnetic tapes, the search for improved lubricating oils, and many other demands from an increasingly complex technologically based society reinforced this requirement. Therefore, from the 1950s onwards the use of synthetic polymers and copolymers, usually of relatively high molecular weights, to provide colloidal 'protection' or stabilisation was increasingly studied. An understanding of the mechanism of this stabilisation came about through the prior understanding of the solution behaviour of polymers.

In this review, the term 'surfactant' or 'surface active agent' is a general description for any molecule that is active at an interface between two immiscible phases. The term 'dispersant' is more specific, and refers only to a molecule that can stabilise a dispersion of finely divided solid particles in a liquid. Similarly, the term 'emulsifier' refers only to a molecule that can stabilise an emulsion of two immiscible liquids. Obviously some surfactants can be quite effective as both dispersants and emulsifiers. Other surfactants are, however, more specific in their behaviour.

This review also concentrates on dispersed systems, solid-in-liquid or liquid-in-liquid, where the continuous phase is an organic solvent or resin solution. It is this area of colloid science that has probably benefited most in recent years from the development of polymeric surfactants.

3.1.1 Polymer solution behaviour and its influence on colloidal stabilisation

In an ideal polymer solution the polymer molecules would show no tendency to associate with each other (i.e. contacts between solvent molecules and polymer molecules are enthalpically favourable) and the polymer molecules would have zero volume. In practice the first criterion is rarely met, and the second is, of course, impossible. However, a tendency towards association between polymer molecules, and the finite volumes of polymer molecules, exert opposite effects on the thermodynamic behaviour of polymer solutions. In consequence, under certain conditions of temperature and solvency the effects are in balance, and the polymer solutions behave in a thermodynamically ideal manner to quite high concentrations. These conditions are known as 'theta conditions' and were first described by Flory in 1949.[1] A solvent or solvent mixture giving theta conditions is therefore a slightly poor solvent for the polymer, since these conditions imply a degree of association between the dissolved polymer molecules.

It has now been demonstrated that in many cases colloidal dispersions stabilised by high molecular weight polymers will flocculate at the theta temperature, or under theta solvency conditions for that polymer. Napper has reviewed this experimental evidence in some detail.[2] A polymer will, therefore, only stabilise a colloidal dispersion when the solvent is a 'better than theta' solvent for the polymer. A key consequence of this behaviour is that any polymeric surfactant will only be effective in a limited range of solvents. It is not possible to devise a universally effective polymeric surfactant.

This process of colloidal stabilisation by polymeric materials is now described by the rather misleading term 'steric stabilisation'.[3] To an organic chemist the term steric implies short range repulsions between nonbonded substituents. However, for the reason described above, steric stabilisation of colloidal systems is essentially a consequence of the thermodynamic behaviour of solutions of polymers. Despite this misnomer the term steric stabilisation is now in normal scientific usage, and will be used throughout this review.

The thermodynamics of colloidal stabilisation may also be subdivided into enthalpic contributions towards stabilisation and entropic contributions towards stabilisation. In nonaqueous solvents, enthalpic interactions between polymer chains tend to be favoured over enthalpic interactions between polymer chains and solvent molecules. Since these interactions can be between polymer chains attached to different particles, they will induce flocculation. Colloidal stabilisation can then only be brought about by the dominance of entropic contributions. These contributions may be pictured as a freedom of movement in polymer chains, which is reduced when two particles approach each other, and the layers of adsorbed polymer start to intermingle. For this reason the molecular weight and the precise structure of a polymeric surfactant can strongly influence the effectiveness of steric stabilisation.

3.1.2 Steric stabilisation versus electrostatic stabilisation

Steric stabilisation and electrostatic stabilisation tend to show different behaviour with respect to the reversibility of flocculation. Figure 3.1(a) shows the potential energy diagram as two electrostatically stabilised particles approach each other. The repulsion generated as the electrical double layers overlap creates a free energy maximum that ensures the particles stay apart. However, if the electrical double layer is compressed by, e.g. raising the ionic strength of the medium, then this maximum disappears and close approach of the particles is energetically favoured (Fig. 3.1(b)). This flocculation effect cannot be reversed by simply lowering the ionic strength of the medium—the particles are now on the wrong side of the energy maximum.

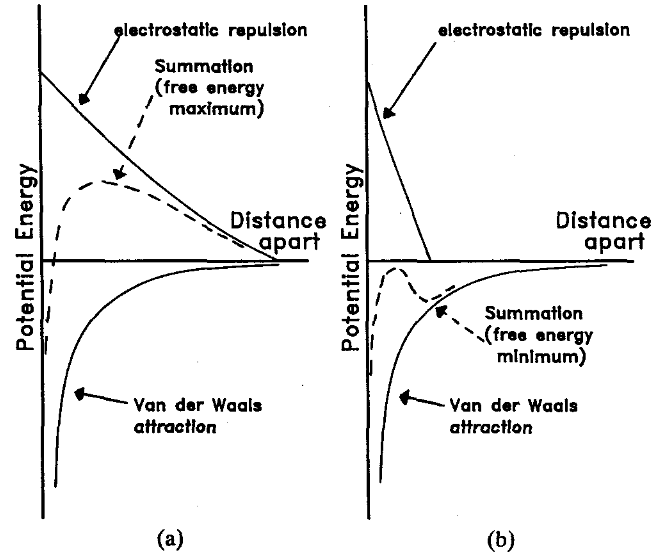

Fig. 3.1 Potential energy versus distance of separation for two electrostatically stabilised particles. (a) Low ionic strength; (b) high ionic strength.

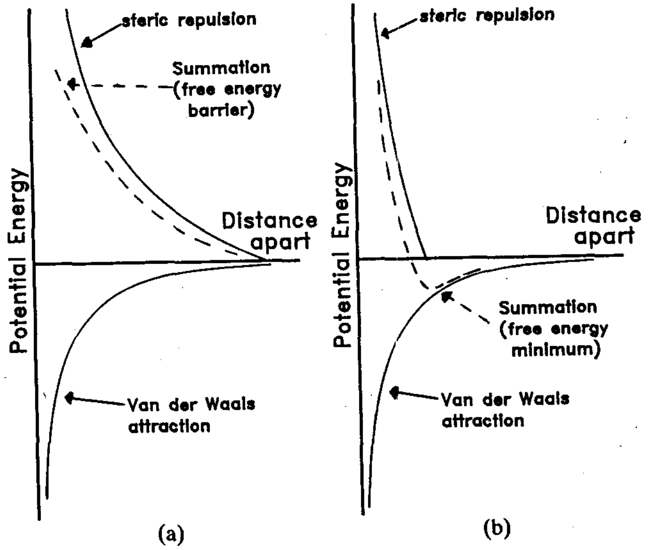

Fig. 3.2 Potential energy versus distance of separation for two sterically stabilised particles. (a) 'Better than theta' conditions; (b) 'worse than theta' conditions.

In the case of steric stabilisation, the layer of stabilising polymer around the particles prevents them from coming into actual contact. Polymer molecules are always present between the two particles. Figure 3.2(a) shows the potential energy diagram for two approaching sterically stabilised particles in a medium that is a 'better than theta' solvent for the stabilising polymer. The steric stabilisation effect of the polymer generates a free energy barrier which keeps the particles apart. When the system is converted to 'worse than theta' conditions, e.g. by addition of a nonsolvent for the polymer, a free energy minimum is generated, and this causes flocculation (Fig. 3.2(b)). However, the particles do not come into actual contact, and reversion to 'better than theta' conditions removes the minimum and causes redispersion.

It is, therefore, generally true that electrostatically stabilised dispersions cannot show reversible flocculation, while sterically stabilised dispersions can show reversibility.

3.2 The design of polymeric surfactants

3.2.1 Influence of molecular weight on steric stabilisation of colloidal particles

Most early work on steric stabilisation by polymers involved the use of high molecular weight polymers, and this led to an assumption that the steric stabilisation barrier was relatively thick, i.e. of a similar order of magnitude to the dimensions of the colloidal particle. More recently both theoretical work[4,5] and experimental studies have shown that for colloidal particles in the most commonly found range of 0·1 to 10 μm, a steric stabilisation barrier of 5 to 20 nm can provide effective stabilisation. Some of the experimental methods used to study the shape of these potential energy curves are particularly elegant and include (i) the use of a surface balance to study the compression of particles sited just inside the oil phase at an oil/water interface,[6,7] (ii) osmotic pressure studies where the dispersion is in a compression cell with a membrane that will only pass solvent molecules,[8,9] and (iii) measurements of the force between two crossed microcylinders coated with the stabilising polymer in solvent.[10]

Any apparent conflict between the high molecular weights of polymers giving steric stabilisation, and the relatively short barrier required to give good steric stabilisation is resolved when the second feature of effective polymeric surfactants is considered. This is the process by which the surfactant is maintained at the interface between the dispersed phase and the continuous phase.

3.2.2 Use of copolymers to give effective anchoring by polymeric surfactants

Homopolymers are, in general, relatively ineffective for imparting steric stabilisation to a colloidal system. This is not surprising in that a polymer chain will tend to prefer either to associate with solvent molecules (a 'good' solvent), or to associate with the surface of the particle (good 'anchoring'). For efficient steric stabilisation both these effects are essential. The stabilising polymer must be held at the interface between the dispersed and continuous phase, and it must also be readily solvated by the continuous phase. Obviously some form of copolymer is likely to best meet these requirements.

Simple random copolymers can be used to increase the interaction between points on the polymer chain and a particle surface. Howard and Ma studied in some detail[11] the adsorption and stabilising effect of copolymers in dispersions of TiO_2 in different solvents. The various copolymers were based on methyl methacrylate with 0·7 to 3·2% of comonomers such as methacrylic acid, vinyl pyridine, acrylonitrile, acrylamide and 2-hydroxyethyl methacrylate. Several samples of TiO_2 with varying surface acidities were used, and in general adsorption and stabilisation were greatest when the comonomer and the TiO_2 surface were of opposing acidity/basicity.

3.2.3 Structural configurations of copolymers giving effective steric stabilisation

We now consider general copolymer configurations that have the potential for giving efficient steric stabilisation; five possible types are shown in Fig. 3.3(a–e). A systematic study of several different configurations of copolymers, all with the same types of comonomers is reported by Jakubauskas.[12] This study confirms that superior surfactants are produced when the steric stabilisation chain is only anchored to the interface at one end, with the other end free to move in the solvent. The choice of configuration when designing a polymeric surfactant depends on both the type of anchor group being employed, and the mechanism of interaction between the anchor group and the dispersed phase. However, in line with Jakubauskas's findings, it appears that polymeric surfactants of the type shown in Fig. 3.3(a), with the solvent-soluble portion in the form of 'loops' (anchored at both ends), rather than 'tails' (anchored at only one end), are less effective.

It is also clear that when the polymeric chains providing the steric stabilisation barrier are only anchored to the interface at one end, they need only contain perhaps 50 to 100 carbon atoms to give a very effective barrier. In the author's experience high molecular weight chains do not enhance the stabilisation.

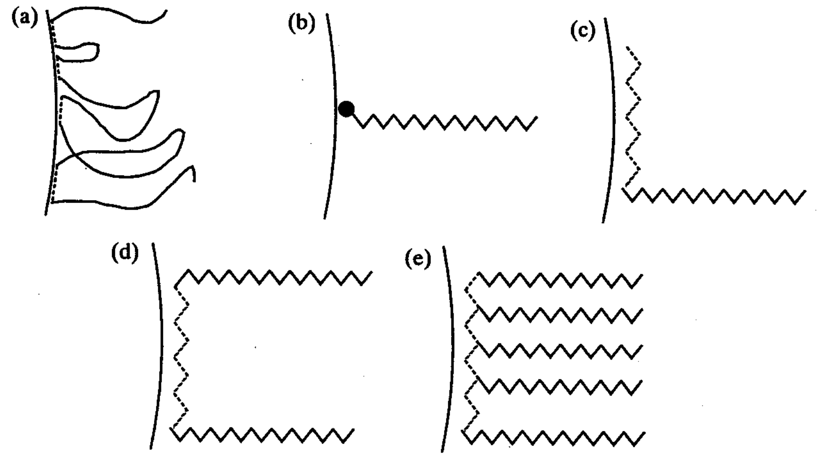

Fig. 3.3 Copolymer configurations giving efficient steric stabilisation of dispersions. (a) Random copolymer; (b) polymer with terminal functional group; (c) AB block copolymer; (d) ABA block copolymer; (e) 'graft' or 'comb' type copolymer.

3.2.4 Commonly used polymers providing the steric stabilisation barrier

Napper lists some of the polymeric chains that are typically used to provide steric stabilisation in both aqueous and nonaqueous systems.[13] Doroszkowski and Lambourne have studied the effect of branching in the steric stabilisation chain, showing that it can be advantageous or disadvantageous, depending on the length of the main chain and its branches, and the position of the branches with respect to the anchoring ends of the chain.[14]

Examination of the patent literature suggests that a limited range of polymers are commonly used to provide steric stabilisation. For stabilisation in very nonpolar organic solvents, particularly aliphatic hydrocarbons, the polyisobutylene chain is frequently used.[15–20] For stabilisation in solvents of higher polarities such as aromatic hydrocarbons, esters and ketones, various polyesters are often used. These polyesters may be based on hydroxycarboxylic acids, with the molecular weight of the hydroxycarboxylic acid governing the range of solvents in which the surfactant is most effective.[21–34] Alternatively, a condensation polyester from a mixture of diacid (or anhydride), diol and a chain terminating acid (or alcohol) may be used.[21,22,24,35,36] A polyethylene oxide chain may be incorporated into polyesters of this type to increase compatibility with the more polar solvents.[37] Poly(methyl methacrylate) is also used to provide steric stabilisation in solvents of higher polarities.[38,39] Finally, polyalkylene oxide chains can be used to give steric stabilisation in the most polar organic solvents such as alcohols, glycols and glycol ethers.[40]

3.2.5 Anchoring mechanisms for polymeric dispersants

3.2.5.1 Ionic and acidic/basic groups A variety of mechanisms can be employed to anchor a polymeric dispersant to a particle surface.[41] At the simplest, and often feasible with inorganic particles, a charged site on the surface of the particle forms an ion-pair bond with the oppositely charged atom or functional group on the dispersant, as illustrated in Fig. 3.4(a). This mechanism is efficient because when the dispersion is in a medium of relatively low dielectric constant, as is the case for most organic solvents, charge separation is not favoured. Many inorganic particle surfaces are also very heterogeneous, with both positive and negative sites. In such cases, dispersants with either negatively or positively charged anchor groups can be equally effective.

A further variant on this mechanism is when the particle surface is acidic (or basic), and protons can be transferred to (or from) a basic (or acidic) anchor group in order to generate an ion-pair bond.

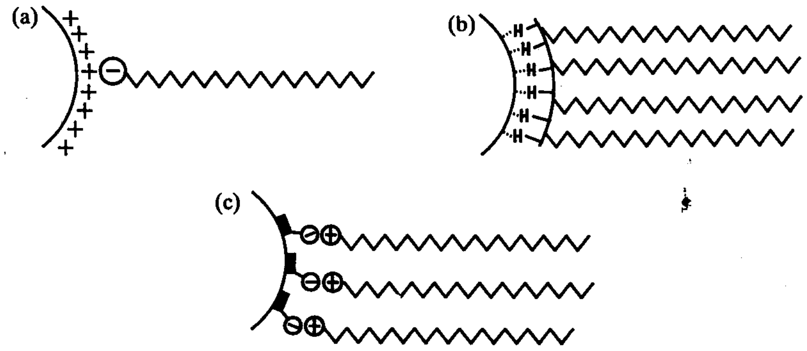

Fig. 3.4 Anchoring: (a) by ion-pair bond formation; (b) by H-bonding to a polymeric group; (c) via a derivative of the dispersed particle.

Examples of functional groups that can be used to anchor polymeric chains to charged or acidic/basic surfaces include amines, ammonium and quaternary ammonium groups, carboxylic, sulphuric and phosphonic acid groups and their salts, and acidic sulphate or phosphate ester groups.[25,26,28,30,35,36,38–40]

The concept of acid/base interactions between pigment surfaces and polymeric materials (particularly resins) has been developed by Sorensen, who has classified 115 different pigments and 39 resins into acidic, basic, amphoteric and neutral categories.[42] This approach was then used to develop a class of polymeric dispersants with polyamide-based anchor groups.[24,31,37]

3.2.5.2 Hydrogen-bonding or polarising groups Most organic particles, and some relatively inert inorganic particles such as quartz, do not have charged sites on their surfaces. They may, however, have H-bond donor or acceptor groups, e.g. ethers, esters or ketones. If, therefore, the dispersant has a polymeric anchor group consisting of many H-bonding groups, although individual H-bonds between particle and dispersant are weak, the overall effect may be one of strong anchoring of the dispersant molecule to the particle, as illustrated in Fig. 3.4(b). Polyamines and polyols are obviously used to give anchoring via this mechanism.[27,29]

A similar situation arises when functional groups are polarised or polarisable. This can also generate a relatively strong anchoring effect between particle and dispersant, an effect which may be difficult to distinguish from the H-bonding mechanism. Polyurethanes are commonly used anchor groups,[21,22,32,33] which may anchor via a polarisation mechanism, although alternative mechanisms have been proposed.[43] Poly(methyl methacrylate) is also frequently used as the backbone in comb type dispersants, and may anchor via this polarisation mechanism. Interestingly, although poly(methyl methacrylate) can act as the anchoring group in e.g. aliphatic hydrocarbons, it can also act as the steric stabilisation chain in more polar solvents.[13]

3.2.5.3 Derivatives of the dispersed particle Some organic particles (phthalocyanine blue pigments are good examples) are not even very responsive to the above anchoring mechanism. In such circumstances the chemical structure of the particle itself may be modified to act as the anchor group. For example, the copper phthalocyanine molecule has been modified by the addition of polymeric chains to give a particularly effective dispersant for copper phthalocyanine pigments.[34] Alternatively, pigment derivatives with substituted ionic groups have been used to activate the surface of the pigment.[40,44,45] The activated surface is then receptive to the charged anchor group of a polymeric dispersant (Fig. 3.4(c)). This approach has been used with mono- and disazopigments where appropriate ionically substituted products may be made by incorporating a proportion of the sulphonated derivative of the pigment coupling component.

The mechanism by which such derivatives anchor on to the particle surface has been postulated as being associated with their large planar structure, which enables Van der Waals attraction forces to act over a large area.[43]

3.2.6 *Polymeric emulsifiers*

The design of polymeric emulsifiers has not been discussed in detail in the literature. Although the criteria for effective steric stabilisation chains are similar in polymeric emulsifiers and polymeric dispersants, the anchoring mechanisms are clearly different. In particular, the anchor group in a polymeric emulsifier is actually dissolved in the dispersed phase rather than attached to the surface. For efficient anchoring, a dissolved polymer chain tends to be especially effective, and, therefore, AB or ABA block copolymers (Fig. 3.5(a) and 3.5(b)) and complex comb copolymers with two different types of attached polymer chains (Fig. 3.5(c)) are the most favoured structures.

Because of the mobility of the liquid–liquid interface, tight packing of polymeric surfactant molecules at the interface is particularly

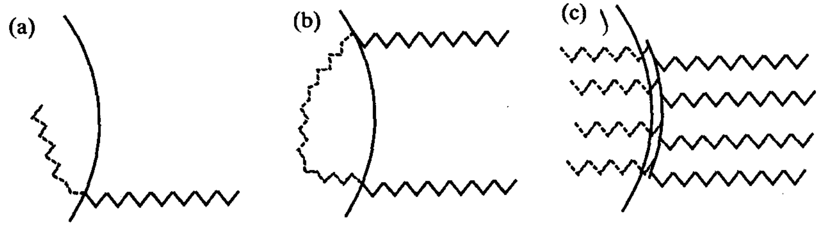

Fig. 3.5 Copolymer configurations giving efficient stabilisation of emulsions: (a) AB block copolymer; (b) ABA block copolymer; (c) complex graft copolymer.

important. For this reason, highly branched polymeric chains tend to be undesirable. Baker has discussed the advantages of polymeric surfactants including situations when both phases of the emulsion are essentially nonaqueous.[46]

For the low-polarity organic solvent-soluble chains in polymeric emulsifiers, polyisobutylene,[18,20,47,48] polyesters based on hydroxycarboxylic acids[23,49] and complex alkyd type polyesters[50] have all been utilised. For water or polar organic solvent-soluble chains, polyalkylene oxides are obviously most commonly used.[23,48,50] Non-polymeric anchor groups that have been proposed include phosphate, sulphate and hydroxylamines.[20,30,48]

3.3 Surface coating applications for polymeric dispersants

3.3.1 Why use polymeric dispersants in surface coating applications?

Perhaps the largest use of polymeric dispersants, and certainly the most widely studied application, is in surface coatings. Despite a movement towards water-based systems, inks and paints (other than decoratives) are still predominantly solvent based. The complex rheological problems associated with spreading, levelling, and then an absence of sagging, together with relatively capital and energy expensive dispersion processes, mean that the use of effective dispersants can offer very significant advantages to the ink or paint maker. Because of the broad range of solvents used, and the even broader range of pigments, a variety of different polymeric dispersants must be used if full benefit is to be obtained. Selection of the most appropriate dispersant is not always simple, and, therefore, the major polymeric dispersant suppliers usually offer a high degree of technical advice and support.

3.3.2 What is a 'good' dispersant?

Even the concept of a 'good' dispersant can cause some confusion. Many users expect an effective dispersant to lower the viscosity of a colloidal dispersion, make it resistant to flocculation and gelling, and give stability to settling. However, the process of reducing particle–particle interactions, which of course reduces viscosity, flocculation and gelling, *can* have the reverse effect on stability to settling. When the dispersed particles are significantly denser than the medium (as is the case with inorganic pigments) they are freer to settle. Even worse, the removal of any tendency to form gel structures means that the settled particles form a particularly dense sediment. Two different approaches can be used to avoid this problem. Either the dispersant can be made or selected so that it is less than perfect, and leaves a weakly structured gel, or a separate thixotrope may be added to the system to generate a weak gel. It is in cases like this where suppliers' advice can be particularly valuable.

3.3.3 Suppliers of polymeric dispersants for surface coating applications

Because suppliers of polymeric dispersants promote their products for different reasons, highlighting different advantages, and because the products are not easily comparable, this review does not attempt to compare different products directly. Rather it attempts to summarise the approaches or concepts identified by the individual suppliers of polymeric dispersants.

3.3.3.1 ICI Colours and Fine Chemicals Group The ICI Colours and Fine Chemicals Group, of Blackley, Manchester, UK, supply a range of polymeric dispersants to the colour using industries under the trade name SOLSPERSE hyperdispersants.

The general advantages obtained from using SOLSPERSE hyperdispersants are:

(1) Dramatic reductions in the viscosities of millbases (see Fig. 3.6).
(2) Improved productivity through higher pigment loadings in millbases, and faster rates of dispersion.
(3) Reduced pigment costs through the development of higher colour strengths (see Fig. 3.7).
(4) Greater manufacturing flexibility through the use of millbases that can be let down into many different resin systems.

The SOLSPERSE hyperdispersant should be selected on the basis of (i) the millbase solvent, and (ii) the pigment. The range of SOLSPERSE hyperdispersants encompasses all the common organic solvents, and Fig. 3.8 shows when the various polymeric hyper-

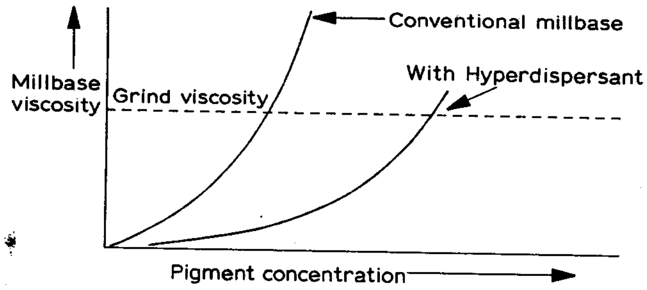

Fig. 3.6 Millbase viscosities—hyperdispersant millbase versus conventional millbase.

dispersants are most effective. It will be seen that although the various products are soluble in a broad range of solvents, they are only recommended for use under 'better than theta' solvent conditions.

SOLSPERSE hyperdispersant technology also makes substantial use of synergistic hyperdispersants to activate the surface of organic pigments that are difficult to disperse, particularly phthalocyanine blues and greens, carbon black, and mono- and disazo yellows. These synergists are insoluble pigment derivatives, and are frequently most effective when predispersed with the polymeric dispersant.

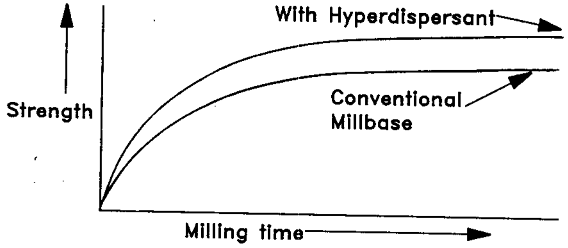

Fig. 3.7 Development of colour strength.

Solvents	SOLSPERSE hyperdispersants			
	3000 9000 17 000	13 000*	24 000	20 000
Aliphatic hydrocarbons	Recommended	Recommended	Insoluble	Insoluble
Aromatic hydrocarbons			Recommended	
Xylene; Butanol, 4:1	Soluble	Soluble		Soluble
Methyl iso-butyl ketone				
Butyl acetate				
Methoxypropyl acetate				
Methyl ethyl ketone				
Ethyl acetate				
Alcohol / acetate blends	Insoluble		Insoluble	Recommended
Butanol				
Butyl cellosolve		Insoluble		
Iso-propanol				
Ethanol				
Ethylene glycol				

*SOLSPERSE 13 000 is only available in solution form.

Fig. 3.8 Selection of SOLSPERSE hyperdispersants.

Ink applications Particular advantages from using SOLSPERSE hyperdispersants in offset ink production are much increased productivity from the labour intensive triple-roll milling process and versatility from the use of one millbase to produce heatset, sheetfed and newsprint inks. SOLSPERSE 17000 is the polymeric dispersant for all the pigments in the offset ink trichromat. It is used alone with rubine toner and red lake pigments, and together with the synergist SOLSPERSE 22000 when dispersing disazo yellow pigments, and with the synergist SOLSPERSE 5000 when dispersing phthalocyanine blue and carbon black pigments. Comparative triple-roll millbase formulations with and without SOLSPERSE hyperdispersants are shown in Table 3.1. A similar combination of SOLSPERSE hyperdispersants can be used in the manufacture of publication gravure inks to obtain higher print densities and sharper, clearer prints, as well as higher productivity.

Packaging inks use a broad range of intermediate and high polarity solvents including toluene, esters, ketones, alcohols and many blends. Packaging gravure inks are generally rich in ester and ketone solvents, where SOLSPERSE 24000 is very effective for dispersing most organic pigments, the synergists SOLSPERSE 5000 and SOLSPERSE 22000 being used when appropriate. Flexographic packaging inks are rich in alcohol, since the presence of stronger solvents such as esters and ketones can damage the flexographic rollers. SOLSPERSE 20000 is then an effective polymeric dispersant, and SOLSPERSE 12000 the synergistic hyperdispersant for activating the surface of phthalocyanine

Table 3.1 Comparative millbase formulations for phthalocyanine blue offset inks

Components	*Conventional millbase* (%)	*Hyperdispersant millbase* (%)
Grinding vehicle[a]	52	35
Alkyd No. 7, isophthalic or urethane	9	9
SOLSPERSE 17 000		2
SOLSPERSE 5000		1
Lutetia Cyanine ENJ (Pigment Blue 15.3)	36	50
Antioxidant	3	3

[a] The grinding vehicle is made up as follows: alkyd, isophthalic or urethane 15%; neutral hydrocarbon resin (m.p. 140°C) 29%; soluble modified phenolic resin 25%; aliphatic distillate 40%.

blue and green, and carbon black pigments. In packaging inks SOLSPERSE hyperdispersants will give bright, glossy and transparent prints without the use of expensive chip preparations.

Paint applications When SOLSPERSE hyperdispersant technology is used in the manufacture of paints, particular advantages are raw material cost savings through the development of substantially higher colour strengths from expensive organic pigments, and the ability of hyperdispersant millbases to be let down into a large variety of different paint resins. In the industrial paint sector one millbase can go into alkyd, alkyd/MF, nitrocellulose, vinyl, epoxy, polyester, thermosetting acrylic and polyurethane resins.

In selecting the appropriate hyperdispersant, its compatibility with the dry paint film must be taken into account as well as its dispersing performance in the solvent. In this respect the requirements for paint applications tend to be more demanding than the requirements for ink applications, as incompatibility can have a deleterious effect on the durability of the paint film. Selection of hyperdispersants for paint applications therefore differs somewhat from selection for ink applications. Table 3.2 outlines the selection in general terms. Table 3.3 gives examples of some typical millbase formulations.

3.3.3.2 BYK-Chemie Gmbh BYK-Chemie Gmbh of Wesel, FRG, supply a range of polymeric dispersants under the trade names ANTI-TERRA, BYK, BYKUMEN, DISPERBYK and LACTIMON. These products are described as additives to solve paint problems, the

Table 3.2 Selection of SOLSPERSE hyperdispersants for use in paint systems

Type of paint:	*Air-drying*		*Industrial finish stoving/baking or chemical cure*
Main solvent:	Aliphatic	Aromatic, ester	Aromatic, ester, ketone
Polymeric hyperdispersant for inorganic and some organic pigments	17 000 13 940	24 000	24 000
Additional synergist			
for organic blues, greens and blacks	5 000	5 000	5 000
for yellows and oranges	22 000	22 000	22 000

Table 3.3 Typical paint millbase formulations

Pigment	%	*SOLSPERSE hyperdispersant*	%	*10% resin solution* (%)
White spirit (aliphatic hydrocarbon) solvent systems				
TIOXIDE TR 92, R-CR2 (Pigment White 6)	80	3 000	1	19
Yellow Iron Oxide 1420 (Pigment Yellow 42)	70	17 000	2·5	27·5
MONOLITE Yellow GN (Pigment Yellow 1)	45	17 000 22 000	3·4 1·1	50·5
MONOLITE Scarlet RN (Pigment Red 3)	55	17 000	5·5	39·5
MONASTRAL Blue FBR (Pigment Blue 15:2)	40	17 000 5 000	3 3	54
Aromatic hydrocarbon, ester or ketone solvent systems				
TIOXIDE TR 92, R-CR2 (Pigment White 6)	80	24 000	1	19
Yellow Iron Oxide 3920 (Pigment Yellow 42)	70	24 000	1	29
Red Iron Oxide 110M (Pigment Red 101)	70	24 000	1·5	28·5
Perylene Red RV6422 (Pigment Red 179)	35	24 000	5·2	59·8
HELIOGEN Blue L7101F (Pigment Blue 15:4)	30	24 000 5 000	3·6 0·9	65·5
Special Black 100 (Pigment Black 7)	40	24 000	4	56

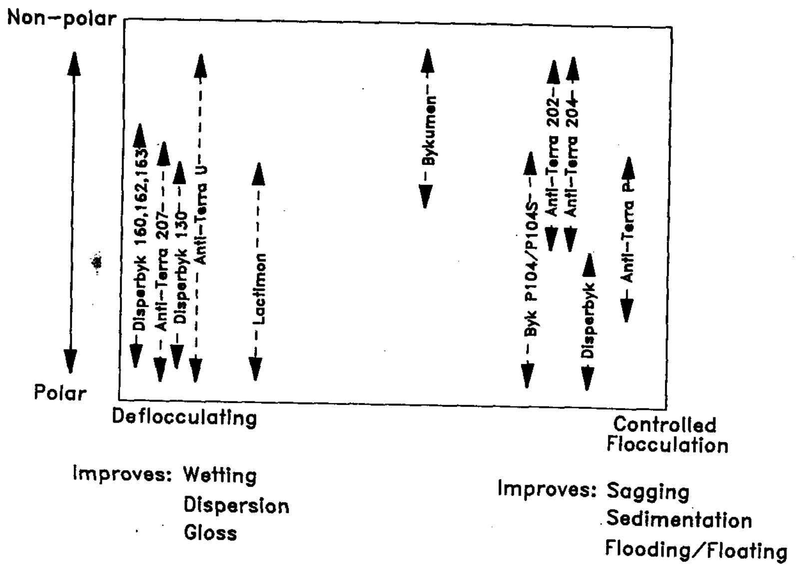

Fig. 3.9 Selection of Byk polymeric dispersants.

main advantages from their use being improved wetting, faster dispersion, better gloss and colour strength, and reduced settling, sagging and flooding. Obviously all these advantages cannot be obtained with one additive, and selection of the most appropriate product should be made on the basis of the balance of effects required, and the polarity of the medium. This can be done by using the matrix diagram shown in Fig. 3.9.

Within the product range, certain dispersants are identified as being especially suitable for certain paint applications, ANTI-TERRA-206 is, for example, recommended for air-drying alkyd systems, and especially for bitumen and antifoulings, and ANTI-TERRA P prevents flooding, floating, and settling in stoving enamels. The DISPERBYK 160/162/163 range of wetting and dispersing additives is designed for high quality industrial, automotive, coil coating and tinting paints. They can stabilise a range of organic and inorganic pigments, and the three products differ in both molecular weight and compatibility. DISPERBYK 160 has the highest molecular weight, and has greatest compatibility with high polarity solvents, while DISPERBYK 163 has the lowest molecular weight and the greatest compatibility with low polarity solvents.

3.3.3.3 DuPont E.I. DuPont de Nemours of Wilmington, DE, USA, supply a range of polymeric dispersants under the ELVACITE trade name. These were originally developed for the automotive paint market, but are now offered for ink, colorant and industrial coating applications. They are described as block copolymers in which one segment associates with the pigment surface, and the other segment provides steric stabilisation.

Advantages obtained from the use of ELVACITE dispersants include the efficient use of colour, efficient dispersion of many less active organic particles, stabilisation of dispersions to shock seeding, high yields from mills due to reduced viscosities, and compatibility with acrylics, acrylourethanes and some alkyds, polyesters and polyurethanes.

It is recommended that, in order to select the most appropriate ELVACITE dispersant, a screening programme to evaluate the interrelated factors (shown in Fig. 3.10) should be carried out. It is critical that all three elements should be considered and that optimum parameters are established prior to manufacturing the paint. The four products in the ELVACITE range are AB 1010, AB 1015, AB 1020 and AB 1030. The pigment interactions and resin compatibilities for the four products are shown in Fig. 3.11.

The range of pigments that an ELVACITE dispersant can disperse in a deflocculated or slightly flocculated state include quinacridones (Pigment violet 19 and Pigment red 122), phthalocyanine blue (Pigment blues 15.1, 15.2 and 15.4), isoindolinone yellow (Pigment yellows 109 and 110), perylenes (Pigment reds 179 and 224), channel blacks and inorganic pigments such as titanium dioxide and iron oxides. An illustration of the dispersing power of ELVACITE

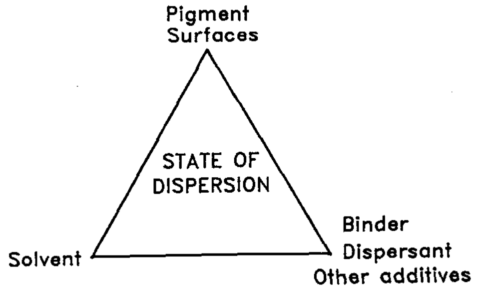

Fig. 3.10 Interrelated factors in dispersion systems.

Pigment interactions	
Product	**Interaction**
AB 1010 AB 1020 AB 1030	Acidic or amphoteric pigment surfaces. Best in aromatic hydrocarbons.
AB 1015	Basic or amphoteric pigment surfaces. Tolerates medium polarity solvents, but aromatic hydrocarbons are best.

Resin interactions		
Product	**Polarity**	**Compatibility**
AB 1010 AB 1015	Least	Copolymers
AB 1020	↓	↑
AB 1030	Most	PMMA

Fig. 3.11 ELVACITE dispersants—pigment and resin interactions.

dispersants is an ability to increase the solids loading of quinacridone magenta dispersions by 25 to 30%. In terms of solvent selection to obtain the maximum effect with ELVACITE dispersants, the least polar aromatic solvent is recommended. Xylene is usually preferred over esters and ketones, while aliphatic hydrocarbons are 'worse than theta' solvents for the steric stabilisation chains. Alcohols cannot be used as, because of their high polarity, they tend to compete with the dispersants for the pigment surface.

3.3.3.4 EFKA Chemicals BV EFKA Chemicals BV of Hillegom, The Netherlands, supply a range of additives for the ink and paint industries, including various polymeric dispersants. EFKA 44 is described as a wetting and dispersing additive for all solvent-containing and solvent-free coating systems, and is particularly suitable for the preparation of bentonite gels. EFKA 64 and EFKA 66 are compatible with a range of binder systems including alkyd/amino resins, nitrocellulose resins, polyurethane systems and acrylics, but not with white spirit or partially white spirit based systems. Both products are wetting and dispersing additives, with the former having the broader compatibility range and inhibiting floating, and the latter inhibiting flooding.

EFKA 46 and EFKA 47 are wetting and dispersing additives designed for use in automotive, coil coating and high quality industrial coating systems. Both products can reduce pigment grinding time and stabilise dispersions, giving consistent colour strength, higher pigment efficiency and reduced flooding problems. EFKA 46 is suitable for inorganic and organic pigments, while EFKA 47 was specially developed for cogrinding pigments, and for use with pigments that are particularly difficult to disperse.

EFKA also supply a dispersing additive for phthalocyanine pigments. This product, EFKA 745, appears to be a phthalocyanine derivative which activates the pigment surface and improves attachment of the polymeric dispersing agent by the mechanism described in Section 3.2.5.3. Claimed advantages include stabilised pigment dispersion, consistent and higher colour strengths, and reduced flooding problems.

3.3.3.5 Kemisk Vaerk Koege A/S Kemisk Vaerk Koege A/S (KVK) of Koege, Denmark, offer a range of hyperdispersants for use in lithographic inks, and these permit thorough wetting and stabilisation of the dispersed pigment phase. These products, sold under the HYPERSOL trade name, facilitate the production of highly concentrated dispersed pigment pastes which can be let down with different varnishes to produce a wide variety of letterpress and offset printing inks. Advantages from using this technology include improved ink performance, increased productivity and flexibility of production, improved colour strength development and reduced stocks of finished inks.

HYPERSOL hyperdispersant technology uses both polymeric dispersants and synergistic dispersants, but unlike other suppliers these are sold in combinations when appropriate. Thus, HYPERSOL L4707 is a fluid preparation containing a synergist and a polymeric dispersant in a high-boiling petroleum fraction, and is designed for manufacturing highly concentrated copper phthalocyanine blue pigment pastes. Similarly, L4708 is designed for use with diarylide yellow pigments. HYPERSOL L4742 and HYPERSOL L4744 are polyester-based polymeric dispersants, and can be used to disperse pigments such as rubine toners and inorganics, which already have active sites on their surfaces.

3.4 Miscellaneous applications for polymeric surfactants

Although surface coatings have, so far, been the main outlet for sophisticated polymeric surfactants, a variety of other interesting applications have started to develop in the last few years. These include both emulsion and dispersion systems, and in some cases even complex formulations that are both emulsions and dispersions. The unifying theme in this review is that the continuous phase is nonaqueous.

3.4.1 *Oil-field applications*

The use of oil-based drilling fluids in oil and gas exploration and extraction has developed enormously in the last 25 years. Oil-based fluids are, in fact, usually invert emulsions with a brine phase emulsified into diesel oil or low aromatic oil, containing a large amount of a dispersed weighting solid (usually barytes) to increase the density. Such fluids are particularly advantageous when drilling deep hot wells, when drilling through water-sensitive swelling clays, and when drilling completion wells.

Drilling fluids must have certain rheological characteristics. Their viscosity must be relatively low, so that the fluid can be circulated rapidly and the drill does not experience too much resistance from the fluid. The fluid must have a reasonable gel strength so that when drilling is stopped the weighting agent and drill cuttings do not settle. However, the developed gel strength must not be too high, otherwise the drill cannot be restarted easily.

Polymeric surfactants can offer benefits to oil-based drilling fluid formulations in two different ways.

(1) Polymeric dispersants can provide rheological control, particularly in high solids content drilling fluids. A high solids fluid may be made up deliberately to cope with high downhole pressure, or may develop through the incorporation of inseparable finely divided drill cuttings. The ICI Specialty Chemicals Group, Everberg, Belgium, offer a polymeric dispersant, HYPERMER OM 1 specifically for this application. Table 3.4 gives a typical formulation to make a barrel of invert emulsion drilling mud. Table 3.5 shows the dramatic effect on rheological properties (as measured by the American Petroleum Institute test methods) when 0·5 lb/barrel of HYPERMER OM 1 is added.

Table 3.4 Typical oil-based drilling mud formulation (to prepare 1 barrel of mud)[a]

Constituent	*Weight*	
	lb	*(kg)*
Diesel oil	300	(136)
Calcium chloride solution (25%)	100	(45·5)
Fatty acid soap	12	(5·45)
Lime	20	(9·1)
Aryl sulphonate wetting agent	2	(0·91)
Bentone	4	(1·82)
Air-blown asphalt	15	(6·8)
Barytes	402	(183)

[a] The density of this mud is 12·3 lb/gal (S.G. 1·48).

Table 3.5 Rheological changes on addition of HYPERMER OM 1 to an oil-based drilling mud

Rheological property	*Control* (*lb*/100 ft^2)	*HYPERMER OM* 1 (0·5 *lb per barrel added*) (*lb*/100ft^2)
Yield point	36	15
Gel strength (10 s)	25	10
Gel strength (10 min)	25	10

Table 3.6 Formulation for high brine content oil-based drilling mud[a]

Component	% (*by wt.*)	*lb*/*barrel*
ICI polymeric surfactant B246	2·58	12·65
ICI polymeric surfactant D477	1·06	5·20
Low aromatic kerosene	18·21	89·25
Calcium chloride solution (25%)	41·23	202·0
Bentone 38	0·52	2·55
Barytes	36·40	178·35

[a] The density of this mud is 11·7 lb/barrel (S.G. 1·4).

(2) For environmental and cost reasons it is desirable to increase the brine content of invert emulsion drilling muds. Polymeric emulsifiers facilitate the formulation of drilling fluids with brine phase contents of 70% or more. In such a formulation a specialised polymeric dispersant may be required to give the desired rheology in the presence of high levels of weighting agent and drill cuttings. The ICI Specialty Chemicals polymeric surfactants B246 and D477 can be used to make high brine content drilling muds, and a typical formulation is given in Table 3.6.

3.4.2 Lubricating oil additives

During the operation of an internal combustion engine, the lubricating oil becomes contaminated with particulate material produced by decomposition of the oil, and with combustion products, including water, penetrating into the lubricating system. These materials tend to form a sludge, which, among other effects, reduces lubricating performance and is corrosive to metal surfaces. Traditionally, metal salts of organic sulphonates and metal alkylphenates have been added to disperse this sludge, but their dispersion performance is not ideal under some operating conditions, and if they decompose they leave metallic residues, which are harmful in their own right.

This led to the development in the 1960s of the so-called ashless dispersants, which are typically amine and polyamine derivatives of polyisobutenylsuccinic anhydride. Specific advantages described include superior sludge dispersion properties at low temperatures, and good rust inhibition in the engine.

There are a substantial number of suppliers of ashless dispersants worldwide, but, in general, they tend to offer dispersion packages that also include other additives to further improve the performance of the lubricating oil. However, some suppliers do offer the ashless dispersants simply in solution in mineral oil, and examples are believed to include PARANOX 105 and 106 from the Performance Products Group of Exxon Chemicals, and LUBRIZOL 890 from the Lubrizol Corporation.

3.4.3 Ceramics

Although water is the most commonly used medium in the fabrication of ceramics, organic solvents are used in certain specialised high performance applications. These are particularly in the field of electroceramics, where many users consider that organic solvents can produce superior thin-film ceramics by the tape casting process, and in engineering ceramics, where the nitride-based ceramic powders can be sensitive to water if used during the slip casting process.

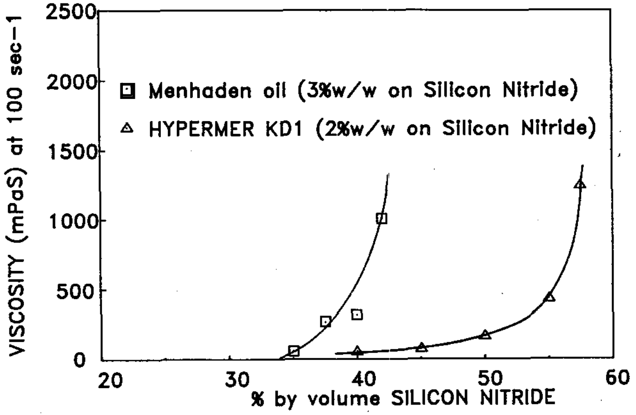

Fig. 3.12 Silicon nitride in methyl ethyl ketone: viscosity versus contraction.

A dispersant is essential when processing with organic solvents, and Menhaden fish oil (a fatty acid glyceride) is most commonly used. The ICI Specialty Chemicals Group have introduced the HYPERMER KD range of polymeric dispersants for ceramic applications. Figure 3.12 illustrates the superior performance of HYPERMER KD 1 when dispersing silicon nitride in methyl ethyl ketone.

3.4.4 Magnetic tapes and discs

Audio and video tapes, as well as floppy and rigid computer discs are normally manufactured by nonaqueous coating processes. The coatings contain high loadings of magnetic particles in durable binders, predominantly urethane resins in the nonrigid systems. The coatings are typically applied from intermediate polarity solvents such as esters, ketones and tetrahydrofuran. Given the poor dispersing power of these binders, a dispersant is required to assist breakdown of the magnetic particle agglomerates and to stabilise individual particles. A fine state of dispersion is needed to produce the desired electromagnetic properties and tape or disc smoothness.

Table 3.7 Video tape—basic formulation

	Weight (g)
Millbase	
Cobalt surface treated Fe_2O_3	40
Dispersant	1·6
Vinyl chloride–vinyl acetate copolymer resin	1·52
Tetrahydrofuran : methyl ethyl ketone (1 : 1)	36·88
Let-down[a]	
Polyurethane resin	8·8
Tetrahydrofuran	35·2

[a] In three stages, with grinding after each stage.

Lecithin, a mixture of fatty acid phosphatides and glycerides has been used by many manufacturers, but recently ICI Specialty Chemicals have introduced a polymeric dispersant, HYPERMER MT 1 for magnetic media applications. A typical formulation is given in Table 3.7. If magnetic tape samples are made to this formulation, using lecithin and HYPERMER MT 1, the latter shows

(i) Higher coercivity (giving better high frequency response).
(ii) Higher squareness (giving higher signal-to-noise ratio).
(iii) Better orientation (giving higher signal-to-noise ratio and reduced crosstalk between tracks).

3.4.5 *Inverse emulsion polymerisation processes*

Many acrylamide polymers and copolymers, which are used, e.g. as flocculants in water treatment and mineral processing and as thickeners in enhanced oil recovery, are manufactured and sold as emulsions of a highly concentrated aqueous polymer solution in oil. These emulsions invert on addition to water and permit much faster dissolution of the polymer than is the case with the equivalent polymer powder. The use of polymeric emulsifiers in the actual acrylamide polymerisation process gives more concentrated and more stable emulsions than use of conventional emulsifiers. Productivity and performance benefits can therefore be achieved. ICI Specialty Chemicals recommend their polymeric surfactants B246 and B261 for use in inverse emulsion polymerisation processes.

A typical process, carried out under nitrogen, involves addition of the aqueous comonomer solution:

Acrylamide/acrylic acid (70/30)	302·7 g
Water	173·5 g
EDTA, sodium salt	0·61 g
Ammonium ferrous sulphate	0·58 g
(pH adjusted to 5·0 with ammonia)	

To a solution of surfactants in oil:

Polymeric surfactant B246	17·5 g
Tween 81*	17·5 g
Paraffinic hydrocarbon	206·0 g

Initiator (1) is added:

Butyl hydroperoxide solution (0·01%)	6·27 g

Initiator (2) is added over 2 h:

Sodium bisulphite solution (0·01%)	9·08 g

to maintain the polymerisation temperature at 40°C. Polymerisation is then completed by addition of:

Sodium metabisulphite solution (30%)	27·23 g

A further surfactant solution:

AEROSOL TR70†	7·5 g
SYNPERONIC NP9‡	5·4 g
Paraffinic hydrocarbon	7·5 g

is finally added as the 'inverting agent' required for when the emulsion is added to water during its end use.

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* TWEEN 81, supplied by ICI Specialty Chemicals, is the condensation product of sorbitan monooleate and 5 moles of ethylene oxide.

† AEROSOL TR70, supplied by Cyanamid B.V., is sodium bis-tridecyl sulphosuccinate.

‡ SYNPERONIC NP9, supplied by the Chemicals and Polymers Group of ICI, is a condensate of nonyl phenol and ethylene oxide.

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4 Surfactant–biocide interactions

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4.1 Introduction

In the UK, the risk of food poisoning has dramatically increased due to:

(a) Changing eating habits, freezer foods, convenience foods, increased poultry and fish consumption.
(b) More communal eating and hence more chance for cross infection.
(c) Cross contamination in the home, caused perhaps by hurried food preparation and careless cleaning down of surfaces.

Keeping the kitchen hygienic means keeping the surfaces both free from dirt and infection. It is pointless to remove soil without eliminating infectious organisms from the surface, and also it is very necessary to remove the types of soil which can harbour and protect bacteria from biocidal action. These problems exist in all institutional establishments such as hotels, restaurants, schools and hospitals, where the risk of cross infection is very high, and where plates and cutlery are washed many times over in one day. Keeping these establishments clean and germ free means using surfactants and biocides together.

Biocides themselves come in a range of chemical types including nitrogen based quaternary ammonium compounds, ampholytes and biguanides such as chlorhexidine. Phenols and chlorinated phenols form another distinct chemical group which has been used extensively before environmental pressures restricted their use in some areas. Another very powerful class of biocide is that based on the halogens, particularly chlorine in the form of sodium hypochlorite and iodine in the various iodophors. Reactive aldehydes like formaldehyde and glutaraldehyde have distinct advantages both as disinfectants and preservatives.

Detergency is the second half of the cleaning equation and whereas quaternary ammonium compounds and ampholytes already have significant detergent action themselves, in other cases it is necessary to add a detergent separately. This is essential to remove any grease, dirt or bacterial slime which may protect bacteria and other living organisms from the action of the cleaning biocide. This would, of course, result in rapid reinfection with consequent risk to health, and in certain industrial applications corrosion can result if pockets of bacterial infection are not removed completely. This is particularly true in oil drilling situations where sulphate reducing bacteria can produce severe corrosion. In choosing a suitable detergent for the cleaning process this product must be compatible with the biocide. It is well known that many biocide–detergent combinations are very effective cleaners and sometimes a synergistic effect is observed whereby the bactericidal efficiency is boosted by this second component. On the other hand, it is equally recognised that many biocide–surfactant combinations are antagonistic and result in a much reduced biocidal efficiency in the cleaner.

Formulation of effective biocidal detergents is a skilful art, which has to take into account many factors such as the presence of alkaline builders and chelating agents which affect the pH of the solution. Other components such as fabric softeners and enzymes are present in laundry cleaners, whereas corrosion inhibitors and solvents may be included in certain industrial products. Formulations have to be devised for the efficient application of a detergent–biocide in industries as varied as food processing, brewing, leather tanning, paint preservation, cosmetics, oil drilling and animal health. In food factories, for example, a foaming detergent is often required which can be applied to vertical surfaces where it sticks in place long enough for effective biocidal action. This is an example of the positive advantage of foam. However, many in-place cleaning processes at breweries or dairies would soon become impossible if efficient foam controlled formulations were not developed. This is also true in the case of dishwashing processes involving great agitation, often in the presence of natural detergents formed by the alkaline hydrolysis of fats and oils in the soil. In some surface cleaning operations the contact time is very short, so very fast acting biocides are essential, whereas slow acting biocides may be satisfactory preservatives.

Choosing the right biocide for certain very sensitive applications is critical. Food contact surfaces must not be cleaned with any chemical combination which is likely to leave behind traces that will taint the food, therefore the rinse-off property of the detergent is of great importance. In the cleaning of breweries, beer pumps and beer lines, it is essential that the detergent and biocide combination do not affect the beer head retention. Certain quaternary ammonium compounds may upset the stability of the protein-stabilised foam. Biocides, which may have some inhibiting effect on cheese making enzymes, are not always allowed in the detergents used for cleaning dairy plant and equipment. In our hospitals, the surgeons and nurses may use surgical scrub formulations to clean and disinfect the hands or other areas of skin. In this case an important consideration is the irritant effect of the biocide–detergent combination.

Having designed and formulated an appropriate composition it is very essential to test its efficiency in some suitable manner. In some instances it is sufficient to control the level of bacteria, fungi or other organisms. This is the biostatic effect which is quite acceptable, e.g. in industrial cutting fluids where considerable levels of bacteria can be tolerated, although there is a danger of resistant organisms developing. This problem would be very much more serious if it occurred in a hospital or in the kitchen. To avoid this possibility it is often necessary to kill all the organisms with the detergent–biocide blend, i.e. a complete biocidal effect is required. In order to work out the maximum safe dilution of the detergent, an appropriate testing method is needed. Different biocides have different kill spectra with regard to the variety of bacteria and fungi encountered, so a suitable test has therefore to be worked out for each chemical type of biocide. The early disinfectants were based on phenolic compounds, and the Rideal Walker test (see Section 4.5.8) was developed for their evaluation. Now that the use of quaternary ammonium compounds is becoming popular, a more appropriate test for this class of material was designed in the form of British Standard Test BS:6471 (see Section 4.2.8).

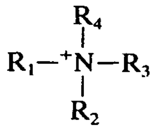
4.2 Quaternary ammonium compounds

4.2.1 General properties

It is appropriate to consider quaternary ammonium compounds first because they are both biocide and surfactant at the same time. Furthermore, their use is increasing in general disinfectant–cleaning formulations, because of their relatively low toxicity. Although a 10% active solution is rather toxic, a typical formulation will only contain 2·5% of active material, to give a QAP100 disinfectant solution, which is regarded as relatively safe. Also, at the normal use dilution of 1000 ppm or less, toxicity problems are unlikely to occur. Long-term feeding studies have also established that there is no chronic toxicity problem, so these materials can be used in the food industry without running any risk from toxic residues. This class of compound is usually considered to be less toxic and tainting than phenols, at the same time being more environmentally acceptable. Furthermore, they do not have the corrosive characteristics of chlorine, the staining problems of iodine, or the rapid deactivation shown by both compounds.[1] Quaternary ammonium compounds have reasonable hard water tolerance, acting very rapidly against both Gram-positive organisms such as *Staphylococcus* spp. and also against Gram-negative organisms such as *Escherichia* and *Salmonella* spp. Reported problems against *Pseudomonas aeruginosa* are not unique to quaternary ammonium compounds as this bacteria is simply hard to kill, being protected by a proteinaceous slime.

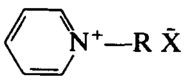
A large variety of structures is possible[2] and four general types are shown below:

A.

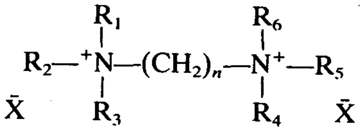


$R_1-{}^{+}\overset{\overset{R_4}{|}}{\underset{\underset{R_2}{|}}{N}}-R_3$

B.

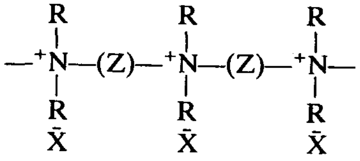


C.



$R_2-{}^{+}\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{N}}-(CH_2)_n-\overset{\overset{R_6}{|}}{\underset{\underset{R_4}{|}}{N}}{}^{+}-R_5 \quad \bar{X} \quad \bar{X}$

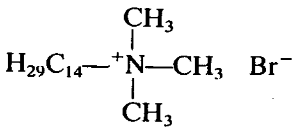
D.



$-{}^{+}\overset{\overset{R}{|}}{\underset{\underset{\bar{X}}{\underset{R}{|}}}{N}}-(Z)-{}^{+}\overset{\overset{R}{|}}{\underset{\underset{\bar{X}}{\underset{R}{|}}}{N}}-(Z)-{}^{+}\overset{\overset{R}{|}}{\underset{\underset{\bar{X}}{\underset{R}{|}}}{N}}-$

where $R = C_1–C_{16}$ alkyl, alkylbenzyl or benzyl; $\bar{X}$ = halogen, $C_2H_5SO_4^-$ or $CH_3SO_4^-$; and (Z) usually contains two to four C atoms.

The well known cetrimide is a typical example of type A.



$H_{29}C_{14}-{}^{+}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3 \quad Br^-$

The biocidal activity is improved by including a benzyl group—the popular benzalkonium chlorides are widely used.

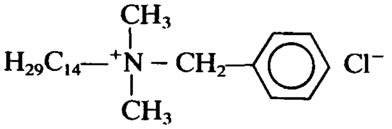
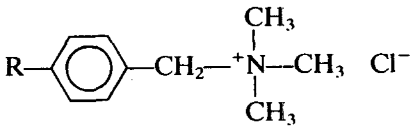


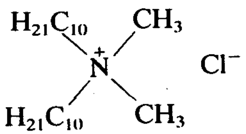
Table 4.1 Comparative bactericidal activity (BS: 6471)

Product	*Bactericidal figure (on 100% actives)*
Cetrimide	1:3 750
Alkyl benzyl dimethylammonium chloride	1:5 000
Alkyl benzyl trimethylammonium chloride	1:5 000
Didecyl dimethylammonium chloride	1:5 000
Didecyl ethyl methyl ethosulphate	1:3 000
Myristyl pyridinium chloride	1:6 000

Alkylbenzyl groups are equally, if not more effective, and are commercially available.



Dialkyl quaternary ammonium compounds of the following structure are becoming increasingly popular perhaps because of their rapid action.



Type B compounds such as myristyl pyridinium chloride are particularly powerful biocides, as illustrated in Table 4.1.

Development of type C biocides has been discouraged by their cost, but polymeric quaternary ammonium compounds of type D have bactericidal, algicidal and fungicidal properties while at the same time being nonfoaming. This special property makes them ideally suited for use in swimming pools, in cooling waters and in other water treatment areas. They may be slower acting than the other quaternary ammonium compounds, but their low toxicity and low irritancy make them valuable members of the quaternary group. Very low dosages, below 25 ppm, are certainly biostatic and algistatic.

The actual alkyl chain length is an important feature. Investigations have shown[3] that alkyl dimethyl benzylammonium chlorides, with an alkyl chain length of 14 carbon atoms, have the optimum biocidal value (see Fig. 4.1). Other evidence suggests that a range of molecular weights can be advantageous, e.g. a blend of C_{12}/C_{14} alkyl dimethyl ethyl benzylammonium halides can show a synergistic effect, enhancing the total biocidal properties.[4]

4.2.2 Anionic interactions

It is well established that the biocidal activity of quaternary ammonium compounds can be destroyed in the presence of some anionic materials, because large molecular weight insoluble complexes

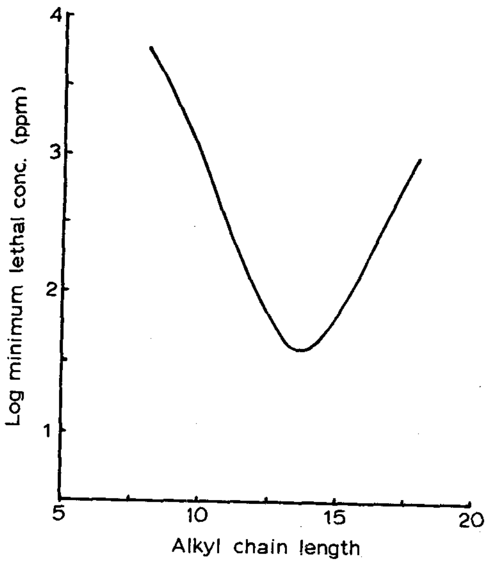
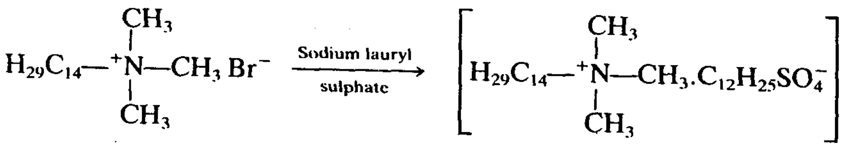


Fig. 4.1 Effect of alkyl chain length: benzalkonium chloride (BAC) versus *P. aeruginosa*.

are likely to form as shown below:



$$\mathrm{H_{29}C_{14}{-}\overset{CH_3}{\underset{CH_3}{{}^+N}}{-}CH_3\,Br^-} \xrightarrow[\text{sulphate}]{\text{Sodium lauryl}} \left[\mathrm{H_{29}C_{14}{-}\overset{CH_3}{\underset{CH_3}{{}^+N}}{-}CH_3.C_{12}H_{25}SO_4^-}\right]$$

This reaction is in fact used in the normal method of analysing quaternary ammonium compounds by a two-phase titration.[5] A little chloroform and dye indicator is added to a solution of sodium lauryl sulphate, and quaternary ammonium compound is titrated in, with frequent shaking, until the chloroform layer is just blue in colour, due to the formation of a solvent-soluble dye–quat complex when the first slight excess of quaternary compound is added. A particularly accurate version[6] can be carried out at pH 9 by using anionic sodium tetraphenyl boron with Bromophenol blue indicator solution. At this pH, amine salt impurity is not measured.

Protein soils are known to deactivate quaternary ammonium compounds to some degree. This is probably because the protein will contain anionic sites which can absorb the cationic quaternary ion. In acid conditions this interaction will be less severe because fewer negative sites should exist in the protein.

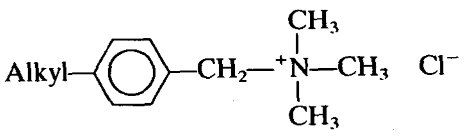
Table 4.2 Cationic–anionic compatibility

Ratio of anionic : cationic	*Bactericidal figure*[a] *(on 100% actives)*
0:1	1:10 000
1:1	1:10 000
1·5:1	1:5 000
2:1	<1:1 000

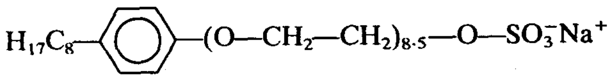
[a] *Pseudomonas aeruginosa,* distilled water, 10 min contact at 20°C.

$$\text{Protein—COO}^- \xrightarrow{\mathrm{H^+}} \text{Protein—COOH}$$

It is interesting to note that, when formulating quaternary ammonium compounds, the presence of certain types of anionic surfactant can be tolerated. If the anionic portion of the surfactant is sufficiently water soluble this can prevent the precipitation of insoluble quaternary complexes. For example, highly ethoxylated anionics have been found to improve cleaning formulations without necessarily deactivating the quaternary compound.[7] This is illustrated in Table 4.2 where the quaternary compound is



and the anionic component is



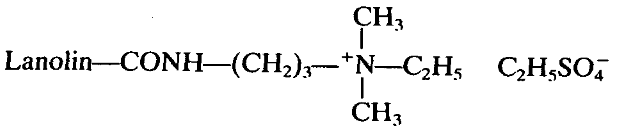
Such a combination would form the basis of a foam cleaner, which may be used, e.g. to clean the surfaces and walls in a food processing factory.

4.2.3 *Interactions with other nitrogen containing surfactants*

It is claimed[8] that cheaper quaternary ammonium biocides can be manufactured if they contain a substantial proportion of tris-(2-

hydroxyethyl) benzylammonium chloride, a low molecular weight compound which is in itself not bactericidal although it does have some algicidal properties. Apparently, a synergistic effect occurs giving rise to a commercially attractive blend. Because this lower molecular weight quaternary compound has low foam characteristics this is in itself an advantage in some applications.

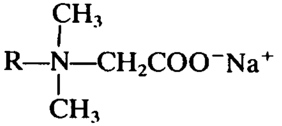
An example of complementary compounds can be found in the use of a benzalkonium chloride biocide together with an emollient quaternary compound. Such a combination can be found in teat dip formulations[9] where the emollient component is a lanolin based quaternary compound as follows:



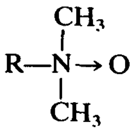
$$\text{Lanolin—CONH—(CH}_2)_3\text{—}{}^{+}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}\text{—C}_2\text{H}_5 \quad C_2H_5SO_4^-$$

Complementary blends of cetrimide and chlorhexidine are well known for their wide biocidal spectrum (see Section 4.4.3). This same idea is embodied in a French patent[10] where a mixture of quaternary ammonium compound and a polymeric hexamethylene biguanide hydrochloride is used in similar hospital applications. Claims for a synergistic effect and a large spectrum of activity lead to formulations for surgical instrument disinfectants. Blends with other surfactants are also recommended for surgical scrubs, claiming a reduction from 10^6 to 10^2 microorganisms/ml after a 1 min contact time (see Section 4.2.7).

Useful surfactant types for increasing the detergency of quaternary based formulations without deactivation are betaines or amine oxides with structures as shown below:



$$\text{R—}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}\text{—CH}_2\text{COO}^-\text{Na}^+$$



$$\text{R—}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}\rightarrow \text{O}$$

$R = C_{12}\text{–}C_{18}$

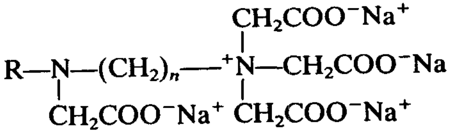
True ampholyte surfactants can also be compatible with quaternary ammonium compounds, but this depends on the number of anionic groups within the molecule. Furthermore, some of these ampholyte structures have good biocidal properties themselves and, being less irritant than quaternary ammonium compounds, useful blends can be used where skin contact cannot be avoided. Ampholytes of the following structure are completely compatible:

$$\text{R—NH—(CH}_2)_n\text{—NH—CH}_2\text{COO}^-\text{Na}^+$$

However, ampholytes with a greater number of anionic groups do show some deactivation[11] as illustrated in Table 4.3.

Table 4.3 Cationic–ampholyte compatibility

Ratio of ampholyte : cationic	*Bactericidal figure (BS: 6471) (on 100% actives)*
0:1	1:5 000
0·3:1	1:5 000
0·6:1	1:4 500
1·2:1	1:2 500



$$\text{R—}\underset{\displaystyle CH_2COO^-Na^+}{N}\text{—(CH}_2)_n\text{—}{}^{+}\underset{\displaystyle CH_2COO^-Na^+}{\overset{\displaystyle CH_2COO^-Na^+}{N}}\text{—CH}_2\text{COO}^-\text{Na}$$

4.2.4 Nonionic interactions

Although it is reported in the literature[12] that low concentrations of nonionic surfactants, below the critical micelle concentration, can have a synergistic effect on the quaternary compounds, nonionic surfactants in general tend to have an inhibiting effect on their biocidal activity. In fact the testing procedure for biocidal efficiency makes use of this deactivating effect of sorbate esters (see Section 4.2.8). A nonionic surfactant is usually added to increase the detergency of the biocidal formulation, so obviously the choice of nonionic surfactant is of great importance to prevent any significant deactivation. Figure 4.2 illustrates the relevant effect of several different nonionic surfactants on alkylaryl trimethyl ammonium chloride when tested against *P. aeruginosa.*[13] An interesting paper by Schmolka[12] explains these results in terms of micelle formation. Above the critical micelle concentration of the nonionic surfactant it is envisaged that the quaternary compound is absorbed into these micelles, being less available therefore for attack on the bacteria. Surfactants which have higher critical micelle concentrations, and therefore less tendency to

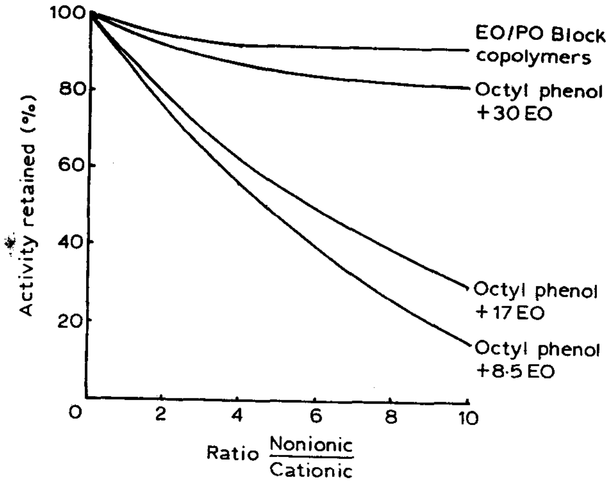


Fig. 4.2 Effect of nonionics on the bactericidal activity of QACs.

form micelles, have a lower deactivating effect; the higher ethoxylates and the ethylene oxide/propylene oxide copolymers are examples of this class. In general, it is advisable to use a ratio lower than 4:1 of nonionic to cationic surfactant to avoid excessive deactivation. This paper further suggests that the synergistic effect of nonionic surface active agents at very low concentrations can be explained in terms of lower interfacial tension and a more rapid passage of the active germicide through the protoplast membrane barrier. It is interesting to note that this type of synergistic effect was reported when using an alkylbenzyl trimethyl ammonium chloride on the Rous sarcoma virus, which causes tumours in chickens. Test results,[14] which showed a marked synergism with an alkyl phenol ethoxylate, are illustrated in Table 4.4.

Direct chemical evidence for this association of quaternary ammonium compound with nonionics in large molecular aggregates has been obtained by Bradshaw *et al.*[15] In this paper, cetyl pyridinium chloride and Polysorbate 80 were the surfactants examined, using an equilibrium dialysis technique. The level of free quaternary ammonium compound in solution, i.e. not complexed with nonionic surfactants, was measured and compared to the biocidal activity of the solution. Results were in accord with the theory that only the active biocide outside the micelle aggregate can be effective against *Escherichia coli.*

Table 4.4 Cationic–nonionic interaction

Type	*Surfactant dilution (actives) showing antiviral activity after 10 min*
Cationic	1:4 000
Nonionic	1:1 000
Blend	1:10 000[a]

[a] This figure refers to the dilution of the cationic.

4.2.5 *Biocidal mechanisms*

The following sequence of events is envisaged when a detergent biocide attacks a bacterium.[16]

1. Absorption into the cell wall is followed by penetration through the largely porous structure. Cationic materials are thought to absorb more strongly because the cell wall is considered to be negatively charged. This might also explain the less toxic effect of anionic detergents because, being negatively charged, they will tend to be repelled.
2. Reaction of the cationic detergent with lipid and protein material in the cytoplasmic membrane. Reaction with the negatively charged carboxyl groups is an obvious site. This causes disorganisation of the membrane molecules. It can cause denaturation and precipitation of protein material.
3. Leakage of low molecular weight components from the cytoplasm can occur, e.g. *E. coli* treated with dilute cetrimide solution leaked potassium ions first, followed by phosphate ions, followed by other material.
4. Degradation of proteins and nucleic acids may occur as a result of attack by the biocidal agent.
5. Eventually, wall lysis can occur, caused by autolytic enzyme activity.

Gram-negative bacteria cells are known to be more resistant to most biocides and in particular to quaternary ammonium compounds. This is now thought to be a result of an extra outer layer of lipoprotein and lipopolysaccharide material, which affords extra protection against antimicrobial agents. It is interesting to note that the use of EDTA chelating agent in formulations will often increase the susceptibility of the bacteria to the biocide. It is thought likely that the EDTA will take calcium and magnesium ions out of this protecting layer, thus

Table 4.5 Cationic–chelating agent interaction

Chelating agent (ppm)	*Bactericidal figure (actives)*		
	EDTA Na_4 (38%)	*NTA* Na_3 (38%)	*HEDTA* (40%)
0	1:2 400	1:2 400	1:2 400
10	1:2 400	1:2 400	1:2 400
100	1:120 000	1:60 000	1:80 000
1000	1:600 000	1:150 000	1:200 000

disrupting its structure and making it more porous so that the attacking biocide can penetrate the cell.[17] Other workers[18] have established that the phospholipid cephalin may be the protecting influence against quaternary ammonium compounds. Evidence has been obtained that two molecules of cephalin react with one molecule of quaternary ammonium surfactant to form an insoluble and inactive complex.

The results shown in Table 4.5 support the view that several chelating agents can improve the biocidal efficiency of an alkylbenzyl trimethylammonium chloride against the Gram-negative organism *P. aeruginosa,* when tested in distilled water with a contact time of 10 min at 20°C.[19] This effect must be distinguished from the improvement in biocidal activity when quaternaries are used in hard water in the presence of chelating agents. It is thought that the hard water cations, calcium and magnesium, may compete with the quaternary ammonium ion on the surface of the bacterium, thus reducing its effectiveness. Chelating agents such as EDTA will, of course, prevent this competition from occurring, so an enhancement of activity can be expected.

4.2.6 *Practical applications*

Biocidal detergents are used in a large number of different applications so the conditions of use can vary enormously. The following short list is given to focus attention on some of these areas.

A. Disinfection of surfaces such as walls, floors, counters, trays, covers, etc. to be found in canteens, kitchens and food shops.
B. Disinfection of equipment and utensils found in the food manufacturing industry and in the kitchen.

C. Disinfection of milk equipment, ice-cream plants, soft drink equipment.
D. Disinfection of refrigerators and other storage areas.
E. Cleaning of hands prior to the handling of food.
F. Disinfection in the poultry industry.
G. Disinfection in abattoirs.
H. Hospital disinfection, including sterilisation of surgical instruments and sterilisation of the skin.
I. Swimming pool disinfection.

Many different components will be put together to form a cleaning formulation, for example EDTA may be included to improve the biocidal efficiency (see Section 4.2.5). Other important factors are mentioned below.

It has been known for some time that certain solvents can enhance the bactericidal efficiency of cationic materials. For example, benzalkonium chlorides can be improved by the inclusion of aromatic alcohols in the formulation[20] and phenyl propanol shows a particularly good effect. A further study at ABM Chemicals[21] showed that many quaternary ammonium compounds were enhanced by the inclusion of certain hydrocarbon or halocarbon solvents in the formulation. Interesting self-emulsifiable disinfectants can be made by the correct blending of quaternary ammonium compounds with nonionic surfactants and suitable solvents. Such a mixture forms a milky emulsion with water and may be used as a general disinfectant in place of the black phenolic type.

The pH at which a biocide detergent is applied can be quite an important factor. It is expected that at higher pH values more negatively charged groups will occur in the bacteria cell wall, e.g. COO^-. Such groups will, therefore, exert a stronger attraction for quaternary ammonium compounds and increase their binding to the surface. There is certainly some evidence that such biocides are rather more effective on the alkaline side, although it must be said that quaternary ammonium compounds can certainly be used in an acid environment, in which they are stable and effective. The chemical stability of quaternary ammonium compounds is sufficient to withstand a certain level of alkalinity, as shown by Table 4.6.

Temperature is always an important factor in chemical reactions. A disinfectant formulation which is ineffective at room temperature may be perfectly adequate at a higher temperature. This effect is well

Table 4.6 Alkaline stability versus *P. aeruginosa*

Quaternary biocide (%)	*NaOH* (%)	*Bactericidal figure*[a]
2·5	0	1:500
2·5	0·4	1:500
2·5	4·0	1:300

[a] After 3 months' storage.

illustrated in some work with benzalkonium chloride against *Staphylococcus aureus* at a pH of 3·5. Figure 4.3 illustrates the rapid increase in efficiency of the biocide as the temperature rises.[22]

4.2.7 Formulations

Quaternary based disinfectants are now governed by British Standard BS:6424:1984 which designates three grades of disinfectant where the QAP number is the recommended maximum use dilution. At this dilution the disinfectant is biocidally effective according to the British Standard Test Method BS 6471:1984 (see Section 4.2.8). Examples of typical formulations:

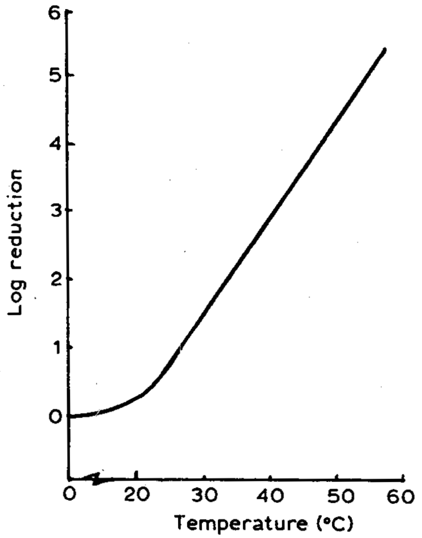


Fig. 4.3 Temperature effect: BAC on *S. aureus*.

	QAP30	QAP50	QAP100
Quaternary biocide (50%)	1·5%	2·5%	5·0%
Nonionic surfactant	1–2%	1–2%	1–2%
Pine oil or fragrance	0·5–2%	0·5–2%	0·5–2%
Water to	100%	100%	100%

For heavy duty cleaning the detergency can be boosted by the inclusion of alkaline builders, chelating agents and cosolvents. A typical QAP100 formulation of this type is:

Quaternary biocide (50%)	5%
Alkyl betaine (40%)	5%
Nitrilotriacetic acid (NTA) Na_3 (38%)	5–10%
Butyl oxitol	2–5%
Water to	100%

The type of powdered product which has been used effectively in dairy cleaning with the Ministry of Agriculture, Fisheries and Food (MAFF) approval would be made up as follows:

Quaternary biocide (50%)	15%
Alkyl phenol ethoxylate	6%
Sodium tripolyphosphate	43%
Sodium carbonate (light)	37%

An emulsifying disinfectant[21] with the biocidal activity enhanced five times by the choice of solvent:

Alkylbenzyl trimethylammonium chloride	10%
Nonionic surfactant	8%
Hydrocarbon oil	67%
Pine oil	5%
Water	10%

A surgical instrument disinfectant:[10]

Biguanide HCl (20% aq.)	20%
Didecyl dimethylammonium chloride	1·5%
Demineralised water to	100%

A surgical scrub:[10]

Biguanide HCl (20% aq.)	1·5%
Ampholyte detergent	15%
Didecyl dimethylammonium chloride	0·02%
Water to	100%

Normal dishwashing machines operate at a temperature of 50° to 70°C with highly alkaline formulations, followed by a rinse cycle at 70° to 80°C to leave the surface spot free and also germ free. Lower temperatures could be used in the washing and rinsing cycles if a biocidal ingredient is put in the rinse aid. Normally the use of quaternary ammonium compounds produces spotting because it absorbs into the glass, giving a hydrophobic surface, thus preventing efficient wetting by other components of the rinse aid. An interesting method of building a formulation for use at 100 to 200 ppm has been reported.[23] The following components are used:

Quaternary ammonium compound as a biocide.
Ampholyte or betaine surfactants to assist wetting.
Nonionic surfactants for foam control.
Large molecular weight hydrophilic polymer to assist the sheeting off action of the rinse aid.

The patent claims excellent results on glass, ceramic and plastic tableware.

4.2.8 *Biocidal testing*

The discovery of ineffective disinfectants on the market resulted in legal proceedings being started by the Consumer Services Departments of the West Midlands and Greater Manchester Councils in 1979. The background to the subsequent development of the British Standard Specification for quaternary ammonium based disinfectants[24] makes it clear that the Rideal Walker Test Method (BS 541), used for phenolic disinfectants, is unsuitable for quaternary based products. Consequently, the British Association for Chemical Specialities (BACS) set out to design a suitable and efficient test method. Variations in test results[25] are illustrated in Table 4.7, which shows clearly the influence of hard water and different contact times on final test figures. Another important factor in the British Standard Test is the presence of organic protein material, which of course can act as a deactivator for the biocide. MAFF testing compares dairy disinfectants with a standard cleaning solution of sodium hypochlorite containing 250 ppm of available chlorine. Experience over the years has shown that certain benzalkonium chloride formulations containing the quaternary ammonium compound at 200 ppm also gave an efficient cleaning action by this standard. Using this as a starting point, BACS eventually developed the following test conditions:

Table 4.7 Different test conditions

	Bactericidal figure vs. E. coli		
	Test 1	*Test* 2	*BS* 6471:1984
Didecyl dimethyl-ammonium chloride (50%)	1:80 000	1:16 000	1:2 500
Alkylbenzyl trimethyl-ammonium chloride (50%)	1:35 000	1:10 000	1:2 500

Test 1—distilled water, 20°C, 10 min contact time.
Test 2—hard water (250 ppm), 20°C, 5 min contact time.
BS: 6471:1984—see text.

BS: 6471:1984
Determination of the antimicrobial value of QAC disinfectant formulations

Disinfectant dilutions	prepared in hard water (200 ppm hardness)
Test organism	*E. coli* ATCC 11229
Temperature	22°C
Contact time	10 min
Organic matter added	5% sterile horse serum
Inactivator	3% Tween 80 + 2% soya lecithin
Result	Based on concentration giving a 99·99% kill.

The test procedure can be summarised briefly as follows:

1. Prepare a series of QAC dilutions in hard water.
2. Inoculate each bottle with *E. coli* in the presence of horse serum.
3. After 10 min at 22°C add to the inactivator mixture which absorbs or otherwise inactivates the quaternary ammonium compound.

4. Plate out a sample of each solution on nutrient agar and incubate at 37°C.

It should be obvious after 48 h which dilutions of the QAC are effective biocides.

4.3 Ampholytes

4.3.1 *General properties*

Some ampholyte surfactant structures have very useful biocidal properties, although compared to quaternary ammonium compounds they tend to be less biocidally active. However, other advantageous properties are described below. A simple example would be the following glycine derivative:

$$R{-}NH{-}CH_2COOOH \quad \text{where} \quad R = C_{10}{-}C_{16}$$

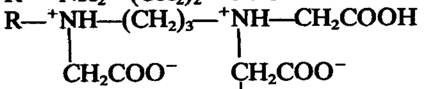
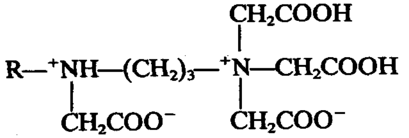
This molecule can exist in three forms depending on the pH.

$$\underset{\text{cation}}{R{-}\overset{+}{N}H_2{-}CH_2COOH} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{zwitterion}}{R{-}\overset{+}{N}H_2{-}CH_2COO^-} \overset{OH^-}{\rightleftharpoons} \underset{\text{anion}}{R{-}NH{-}CH_2{-}COO^-}$$

The molecule exists in the zwitterion form at a certain pH value called the isoelectric point, or to be more accurate, in a certain pH region where aqueous solubility is at a minimum. Table 4.8 shows a range of structures with the corresponding isoelectric points.

Not all ampholyte structures are significantly biocidal although they may be excellent surfactants. Biocidal activity seems to be enhanced as the number of nitrogen atoms increases, as shown in Table 4.9. The excellent surface active properties of this class of compound can reduce the surface tension of water from 72 dynes/cm to 30 dynes/cm with a concentration of only 0·03% ampholyte. It is, therefore, to be expected that the penetrating power and detergency of these materials should increase their antimicrobial effectiveness. In fact, some work has been carried out[26] using bacteria which have been fully treated with ampholyte surfactants before subsequent exposure to a range of biocidal materials. Increased effectiveness of the biocide was noted in most cases.

Table 4.8 Structure and isoelectric range

Structure	*Isoelectric region (pH)*
$R{-}NH{-}(CH_2)_2{-}NH{-}(CH_2)_2{-}{}^{+}NH_2{-}CH_2COO^-$	8·2–9·1
$R{-}NH{-}(CH_2)_3{-}{}^{+}NH_2{-}CH_2COO^-$	8·5–9·5
$R{-}{}^{+}NH_2{-}(CH_2)_2{-}COO^-$	4·0–4·5
 $R{-}{}^{+}\underset{CH_2COO^-}{NH}{-}(CH_2)_3{-}{}^{+}\underset{CH_2COO^-}{NH}{-}CH_2COOH$	1·5–3·2
 $R{-}{}^{+}\underset{CH_2COO^-}{NH}{-}(CH_2)_3{-}{}^{+}\overset{CH_2COOH}{\underset{CH_2COO^-}{N}}{-}CH_2COOH$	0·7–2·7

R = coco alkyl.

A list of advantages claimed for some ampholyte surfactants includes effectiveness as a bactericide, fungicide and virucide and in addition they are odourless and deodorising. Furthermore, they are effective in the presence of soils, in particular protein; they are easy to handle, being relatively nontoxic, and noncorrosive to metals and other materials. These properties are particularly useful in areas such as the cleaning and disinfecting of dairy plant and equipment, breweries, soft drink bottling plants and slaughterhouses and for general surface cleaning and disinfection in food areas.

Because of their low toxicity ampholytes have even been recommended for use in hospitals as instrument disinfectants and surgical hand washes. Claims are made for the effectiveness of ampholytes against many different organisms[27] although there is a certain amount

Table 4.9 Structure and biocidal activity

Structure	*Bactericidal action*[a] *(min)*
$C_{12}H_{25}NHCH_2COOH$	10
$C_{12}H_{25}NH(CH_2)_2NHCH_2COOH$	5
$C_{12}H_{25}NH(CH_2)_2NH(CH_2)_2NH\ CH_2COOH$	1

[a] 0·05% solutions vs. *S. aureus*

Source: G. Sykes, *Disinfection and Sterilisation*, 2nd edn, pp. 377–8, 1965.

of contradictory evidence concerning their activity, which seems to depend on the test method being used. For example, an ampholyte, a benzalkonium chloride quaternary compound and a cresol disinfectant were compared against *Paramecium cordatum* to give results after 10 min contact, suggesting an order of activity of quaternary ammonium compound, ampholyte, then cresol. After 30 min contact time the quaternary compound and ampholyte were equally effective. There is evidence[28] that ampholytes are effective against spores given sufficient time, e.g. *Encephalitozoon cuniculi* were inactivated by 0·1% ampholyte in 30 min. Like other cationic disinfectants, ampholytes are also effective against many lipophilic viruses, and effectiveness against Newcastle disease virus and Aujeski's disease virus makes this type suitable for use in disinfecting animal houses. Unlike cationic quaternary ammonium compounds the ampholytes are unaffected by hard water and solvents such as alcohol.

4.3.2 Anionic interactions

Ampholytes are considered to have very low toxicity with particularly low skin and eye irritation. This makes them very suitable for use in shampoo formulations where they also detoxify the rather harsh anionic components. It is thought that the mixed micelle prevents the irritant anionic from absorbing into the skin surface. Unfortunately, this mixed micelle formation usually inactivates the biocidal activity. For example, a 5% ampholyte solution tested by the method of BS:6471 had its biocidal activity reduced below 50% by the addition of 2·5% of alkyl ether sulphate[29] containing 4·5 moles of ethylene oxide. Increasing the ethylene oxide level to 17 moles produced an ether sulphate which did not deactivate.

4.3.3 Interactions with other nitrogen containing surfactants

An article[30] has been published which claims a synergistic effect for an ampholyte used with chlorhexidine in the treatment of dental plaque. Laboratory work[31] has also established a useful synergistic blend of an ampholyte and a nonbiocidal betaine. The results illustrated in Table 4.10 were obtained against *E. coli* in the presence of horse serum and hard water, with a contact time of 15 min. The optimum formulation has good biocidal efficiency coupled with improved detergency from the betaine component. Furthermore, this combination should have very low toxicity and very low skin and eye irritancy, and as an extra advantage the betaine prevents the ampholyte from precipitating out within its isoelectric region. Presumably it is solubilised by some mixed micelle formation.

Table 4.10 Betaine synergism

Ampholyte (%)	*Betaine (%)*	*Total actives (%)*	*Biocidal figure*
0·0	32·5	32·5	<1:50
32·5	0·0	32·5	1:600
14·5	18·0	32·5	1:800
12·5	20·0	32·5	1:600
10·5	22·0	32·5	1:500
8·5	24·0	32·5	1:400
6·5	26·0	32·5	1:300

Compatibilities of dodecyl aminopropionic acid in its different forms have been studied[32] by adding stoichiometric quantities of anionic, cationic and nonionic surfactants at different pH values with respect to the isoelectric region. This avoids errors due to resolubilisation when either reagent is in excess. The results are shown in Table 4.11 where the complete compatibility, i.e. lack of precipitation with cationic surfactants at all pH values, is indicated. Further studies showed that a mixture of hexadecyl trimethylammonium bromide and dodecyl aminopropionate were still biocidally active in solution, proving that no detrimental interaction was occurring. It is interesting to note that isolation of hexadecyl trimethylammonium dodecyl aminopropionate as a separate salt gave rise to very different surfactant properties, in spite of this very large molecule being soluble in water, and it was

Table 4.11 Compatibilities in solution

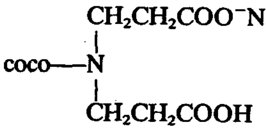
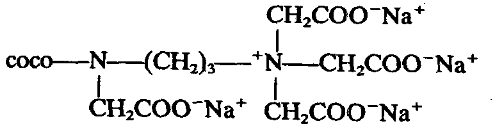
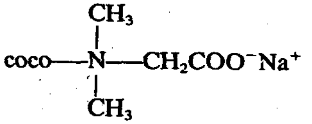
Ampholyte	*Anionics*	*Nonionics*	*Cationics*
Acid salt	Incompatible	Compatible	Compatible
Zwitterion	Compatible (except sulphonates)	Compatible	Compatible
Alkali salt	Compatible	Compatible	Compatible

found to be biocidally inactive in this form. The results in Table 4.11 also indicate compatibility of anionics and ampholyte at alkaline or neutral pH conditions. Again, no precipitate is observed but biocidal inactivation may still occur by mixed micelle formation.

4.3.4 Nonionic interactions

The effect of nonionic surfactants does not seem to have been extensively studied, but presumably some deactivation may be expected if mixed micelles are formed, thus hindering the absorption and penetration of the biocidal material when in contact with the bacteria.

Table 4.12 Hydrotrope effect

Structure	*Actives required (g)*[a]
 $\text{coco—N}(\text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+)(\text{CH}_2\text{CH}_2\text{COOH})$	0·12
 $\text{coco—N}(\text{CH}_2\text{COO}^-\text{Na}^+)\text{—(CH}_2)_3\text{—}^+\text{N}(\text{CH}_2\text{COO}^-\text{Na}^+)_2\text{—CH}_2\text{COO}^-\text{Na}^+$	0·21
 $\text{coco—N}(\text{CH}_3)_2\text{—CH}_2\text{COO}^-\text{Na}^+$	0·7

[a] To give a clear solution of 2 g octylphenol + 8·5 EO in 100 ml of 3% NaOH at 25°C.

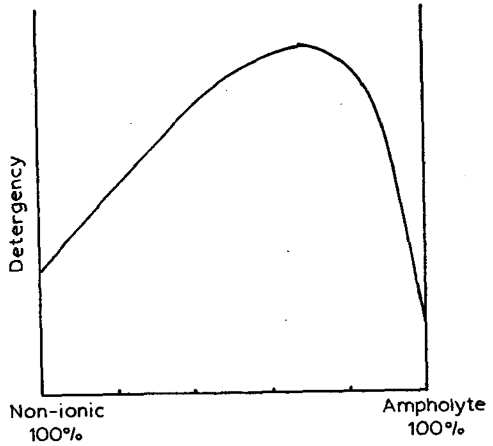
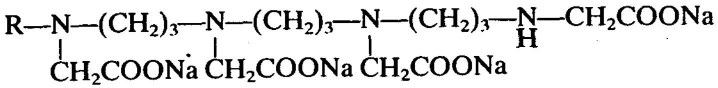


Fig. 4.4 Synergistic detergency.

The hydrotroping ability of ampholytes is a useful, practical effect which can save money in formulating highly built concentrated formulations such as liquid detergents for laundry products. Comparative results[33] are shown in Table 4.12. A further advantage of using the blend of nonionic and ampholyte surfactant is observed when the detergency is measured. It has been found that a significant synergism exists which depends very much on the ratio of nonionic to ampholyte present in the formulation.[34] This is illustrated in Fig. 4.4 where a ratio of 2:1 in favour of the ampholyte seems to be the optimum combination for this particular type of surfactant described as an alkyl polyamphocarboxyglycinate. For example,



$$\text{R—N}(\text{CH}_2\text{COONa})\text{—(CH}_2)_3\text{—N}(\text{CH}_2\text{COONa})\text{—(CH}_2)_3\text{—N}(\text{CH}_2\text{COONa})\text{—(CH}_2)_3\text{—NH—CH}_2\text{COONa}$$

A patent[35] describes the potential use of this type of biocidal ampholyte in many cleaning formulations, including liquid laundry detergents.

4.3.5 Biocidal mechanisms

It is expected that the mechanism of attack by ampholyte surfactants is rather similar to that described for quaternary ammonium compounds (Section 4.2.5). In the first place, absorption into the cell wall is expected, followed by penetration to the cytoplasmic membrane where interaction is likely to occur between the surfactant, lipid and protein material. If this theory is correct it is expected that the pH will have a large influence because of its effect on molecular charge. Some evidence has been obtained to support this view, using dodecyl aminopropionic acid.[36]

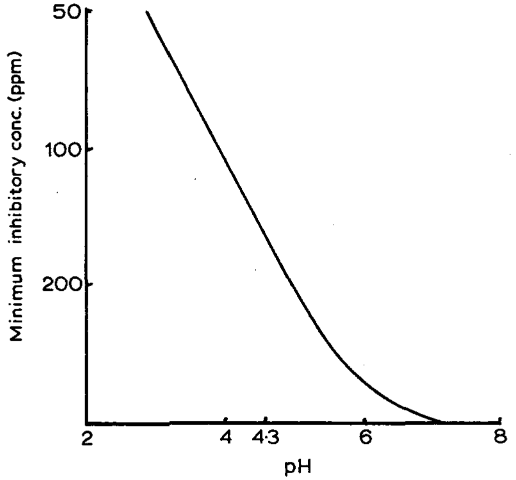


Fig. 4.5 Biocidal activity versus pH.

Figure 4.5 illustrates the increase in activity of this ampholyte against *P. fluorescens* as the pH becomes lower and therefore as the molecule becomes increasingly cationic. Below the isoelectric point of pH 4·3, its activity approaches that of a similar sized quaternary ammonium compound. Further work is discussed in the same monograph,[36] which shows that the situation is not so simple. Using molecules with an increasing number of nitrogen atoms, the bactericidal effect can be greatest around the isoelectric region and, furthermore, the dependence on pH becomes much less. It has been shown that ampholytes tend to be less deactivated in the presence of protein than are quaternary ammonium compounds and this could well be another indication that the mechanism of attack is slightly different.

4.3.6 Practical applications

In the general cleaning applications appropriate to ampholyte surfactants, various conditions are encountered which may affect the biocidal efficiency. In many areas the excellent wetting and detergency of this class of compound makes them a preferable choice to quaternary ammonium compounds. In addition to pH effects the presence of chelating agents is another important factor. For example, an alkaline formulation containing 2·5% ampholyte plus 10% NTA Na_3 can have a biocidal activity three times that observed in a similar formulation containing only 4% NTA Na_3.

It has already been stated that this type of biocide is less affected by protein than are other cationic materials such as quaternary ammonium compounds. For example, it has been reported[37] that the bactericidal activity of an ampholyte was reduced three to four times by the presence of milk, whereas several quaternary ammonium compounds suffered a 20 to 50 times reduction in their biocidal effectiveness. This property makes ampholytes ideal surfactants for use in dairy cleaning, for equipment such as milk tanks and cans, pipes, hoses, pumps, heaters, coolers and separators. It can also be used for hand washing or the cleaning of boots and clothing which may be used in the dairy. Where milk products are used for cheese manufacture, it is essential that traces of biocide do not interfere with the cheesemaking process. Efficient rinsing brings down the concentration of ampholytes well below the level at which this interference can occur, whereas quaternary ammonium compounds are more tenacious and may not be completely removed.

The low toxicity of this type of surfactant is reflected in the fact that ampholytes have FDA approval in certain areas, e.g. in Part 175 Indirect Food Additives: Adhesive Coatings and Components, an ampholyte of the following structure is mentioned:

$$C_{14}\text{–}C_{18}\ \text{alkyl—NH—(CH}_2)_3\text{—NH—CH}_2\text{COONa}$$

Ampholytes are also claimed to provide good protection against the bacteria and other organisms found in meat products, e.g. salmonella, beef trichophyta, chicken aspergilli, swine fever virus, Newcastle disease virus and several others. This means that this type of bactericide can be used in the cleaning and disinfection of food processing factories, poultry farms and slaughterhouses and in most aspects of food production.

In the brewing industry, special problems exist in controlling wild yeasts, bacteria and moulds, which may interfere with the fermentation process. Ampholytes are reported to be effective biocides in this respect.[38] A distinct advantage is observed over quaternary compounds in that traces of the biocide which may finish up in the beer are less likely to produce turbidity or haze. Furthermore, there is very little effect on beer head retention, whereas the interaction of quaternary biocides and the beer head forming proteins can be quite marked. The adsorption of ampholytes on to surfaces, and therefore their resistance to subsequent rinsing, will be pH dependent, but in the normal alkaline formulations this should not be a problem because the molecule will be in the anionic state.

The low toxicity and low skin irritancy makes this class of compound ideal for incorporation into hand cleaners, particularly as it is not affected by the hardness of the water. Various tests[39] have indicated its effectiveness against the types of organism found in hospitals and it has, in fact, been tested as a component of surgical scrub formulations.

4.3.7 Formulations

The following suggested formulations[40] are designed to obtain the maximum biocidal efficiency from an ampholyte surfactant. Biocidal efficiency testing was carried out according to the British Standard Method for Quaternary Ammonium Biocides, BS:6471. This would seem to be an appropriate method in view of the similar biocidal mechanism.

(a) 10% active ampholyte—bactericidal figure 1:160.

(b) Biocidal hand wash

Ampholyte actives	1·75%
Betaine actives	2·8%
Thickener	2–5%
Water to	100%

Biocidal figure 1:60
Expected biocidal figure 1:28

The synergistic effect of the betaine is observed.

(c) Biocidal dishwashing liquid

Ampholyte actives	5%
Betaine actives	7%
Sulphonated alkyl phenol ethoxylate	1·5%
EDTA Na_4	0·2%
Thickener	5%
Water to	100%

Biocidal figure 1:160
Expected biocidal figure 1:80

Here again, the synergism of the betaine is observed.

The other feature is the inclusion of a foamy anionic surfactant without producing any deactivation. This is possible if the level of ethoxylation is sufficiently high (see Section 4.3.2).

(d) Biocidal liquid laundry detergent

Ampholyte actives	2%
Betaine actives	3·2%
NTA Na_3	15%
Blend of alcohol ethoxylates	6·5%
Hydrotrope	2%
Sodium metasilicate $5H_2O$	4%
Water to	100%

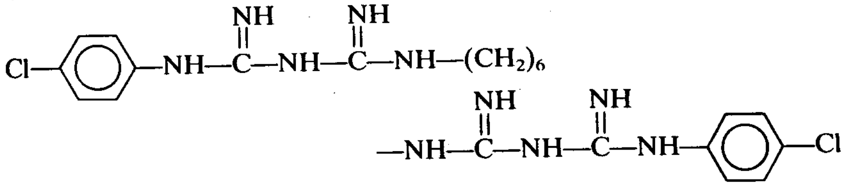
Biocidal figure 1:100
Expected biocidal figure 1:32

Here we are seeing the synergistic effect of both the betaine and the NTA, producing a very satisfactory biocidal formulation which will require further modification to include other ingredients such as soil anti-redeposition agents and possibly an optical brightener.

4.4 Chlorhexidine

4.4.1 General properties

Another cationic biocide in common use is chlorhexidine in the form of one of its salts.



This material is not significantly surface active because it lacks large fatty groups in the molecule, consequently, to get the best disinfecting effect it is normal to combine it with selected surfactants. The best choice of surfactant and the difficulty of formulating is discussed in later sections.

This material is often preferred for hospital use because it lacks the known toxic hazards of phenols and it does not possess the potential neural toxicity of hexachlorophene. Subsequent discussion will also show that it has certain advantages over the other antiseptic surfactant combination in general use, namely the iodophor (see Section 4.4.6). The high level of antibacterial activity shown by chlorhexidine and its salts, plus the strong binding to the skin to give persistence of action, coupled with the general low toxicity of the material, makes the product ideal for topical application. Furthermore, absorption through the skin is absent or negligible. In this respect it is much better than hexachlorophene which can absorb to dangerous levels. Formulations for hospital use have FDA approval in the USA because it is possible to formulate surfactant blends without an unacceptable increase in the irritancy. Such products are used extensively to treat mucous membranes and damaged tissue as well as being ideal for cleaning surgical instruments.

Chlorhexidine base is virtually insoluble in water and most of its salts also have a very low aqueous solubility, e.g. the dihydrochloride salt and the diacetate salt have solubilities of 0·06% and 1·9% at 20°C, respectively. These salts are normally used in alcoholic solution or in powder formulations. The most convenient material is the digluconate salt which can be made at a 20% aqueous concentration for easier formulation.

$$C_{22}H_{30}Cl_2N_{10}.2HOCH_2(CHOH)_4COOH$$

This salt is only stable in the range pH 5–8. Above pH 8 the free base will be precipitated and hydrolysis can occur to produce unwanted *p*-chloroaniline. Fortunately, this pH range is ideal for skin application.

4.4.2 *Anionic interactions*

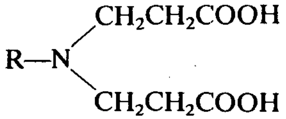
Chlorhexidine salts generally behave as cationic materials, rather like quaternary ammonium compounds. They are, therefore, incompatible with most anionic surfactants, forming an insoluble or inactive combination. However, exceptions to this rule are claimed in a European Patent.[41] This patent claims the manufacture of chlorhexidine salts of various anionic and ampholyte surfactants. For example, alkyl ether carboxylates,

$$R\text{—}O\text{—}CH_2(CH_2\text{—}O\text{—}CH_2)_n\text{—}COOH$$

alkyl ether sulphonates,

$$R\text{—}O\text{—}(CH_2\text{—}O\text{—}CH_2)_n\text{—}CH_2CH_2\text{—}SO_3H$$

N-alkyl iminodipropionates,



$$R\text{—}N\begin{matrix}\diagup CH_2CH_2COOH\\ \diagdown CH_2CH_2COOH\end{matrix}$$

and alkyl derivatives of hydrolysed protein material, suitable for use in the cosmetics industry. These combinations are claimed to have the bactericidal effect of the chlorhexidine coupled with the surfactant properties of the anionic component. Test results against four organisms, shown in Table 4.13, indicate that in three cases there is, in fact, an enhanced biocidal effect. Evidence also shows that the low skin and eye irritation of the chosen surfactants is maintained in their chlorhexidine salt form. Furthermore, the oral toxicity of these novel salts is rather low.

Table 4.13 Chlorhexidine–anionic surfactant salts: biocidal concentrations (mg/ml)

	S. aureus	E. coli	P. aeruginosa	Candida albicans
Chlorhexidine digluconate	0·12	0·06	16·0	31·2
Alkyl ether carboxylate (acid)	1·56	12·5	6·2	50·0
ACE salt of chlorhexidine	0·56	0·035	2·8	5·6

Useful salts of chlorhexidine have been made by a combination of the base with an anion derived from sequestering aminocarboxylic acids. Although EDTA forms very insoluble combinations, several common sequestering agents of this type have been combined with chlorhexidine to make reasonably water-soluble derivatives with exceptionally good bactericidal properties. It is claimed[42] that more potent biocides can be made this way, killing a wider range of organism. A particularly effective combination is achieved by reacting chlorhexidine base with *N*-hydroxyethyl ethylenediamine triacetic acid (HEDTA). The preferred combination is in a 2:1 ratio of HEDTA:chlorhexidine base. The results shown in Table 4.14 illustrate the superior biocidal activity of the di-HEDTA salt compared to that of the digluconate salt. These tests were carried out according to BS 3286:1960, using very stringent conditions with the highly resistant Gram-negative bacterium *P. aeruginosa* in the presence of hard water and bovine serum, and a contact time of 5 min.

Table 4.14 Chlorhexidine di-HEDTA salt: survivors per million bacterial cells

	Bactericide concentration (ppm)						
	200	300	400	600	800	1 000	1 250
Chlorhexidine digluconate	uc	uc	uc	uc	3 627	1	0
Chlorhexidine di-HEDTA	21 818	2 909	16	0	0	0	0

uc—uncountable number of survivors.

4.4.3 *Interactions with other nitrogen containing surfactants*

Some of the difficulties involved in formulating chlorhexidine salts into useful mixtures are discussed in Section 4.4.6. It will be seen that it is usually necessary to add surfactants to the formulation not only to increase general detergency but also to prevent precipitation of insoluble chlorhexidine compounds, particularly in the presence of hard water. Betaines are very suitable compatible surfactants, and amine oxides can be particularly useful when they also add viscosity or body to a liquid formulation. In a hospital scrub or skin cleaner, viscous liquids are preferred for ease of application without undue spilling of the material. These surfactant types are known to be mild to the skin with very low irritation characteristics.

Further interesting results are shown in Fig. 4.6, which illustrates the synergistic effect of adding a quaternary ammonium compound, namely didecyl dimethylammonium chloride, to the di-HEDTA salt of chlorhexidine. These results were again obtained using *P. aeruginosa*. If the bactericidal effect of the two biocides was merely additive then the straight line A would be observed. However, the results are plotted on curve B which definitely shows the synergistic effect of the quaternary ammonium compound, i.e. smaller quantities of the mixture are required to kill the bacteria than are anticipated. Adding the quaternary ammonium compound also increases the cleaning power and the detergency of the formulation, when it is used as a skin antiseptic. Furthermore, it is able to solubilise the less soluble chlorhexidine salt to an acceptable concentration for such a use. The solubilising power of various quaternary ammonium compounds is illustrated below—

18% cetrimide solubilises 27% chlorhexidine/HEDTA salt;

30% benzalkonium chloride solubilises 15% chlorhexidine/HEDTA.

This synergistic biocidal effect is observed with a range of quaternary ammonium biocides, thus illustrating the very effective combinations which can occur between biocides and certain compatible surface active agents.

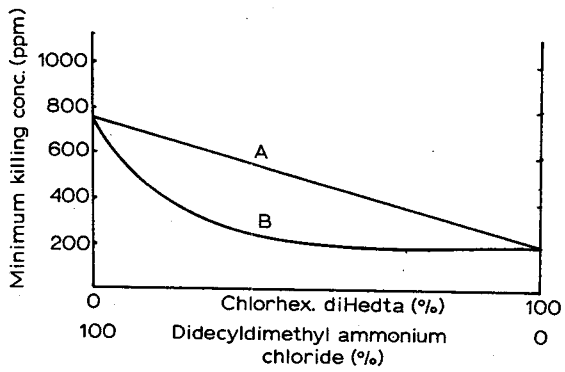


Fig. 4.6 Synergistic blend.

4.4.4 *Nonionic interactions*

In some circumstances, addition of a nonionic surfactant to chlorhexidine formulations can increase the biocidal effect, presumably for the same reason given for quaternary ammonium compounds (see Section 4.2.4). The nonionic is thought to have increased the penetration of the chlorhexidine into the cells so that it can reach the cell membrane and cause damage. This effect is normally observed only at very low surfactant concentrations. Octyl phenyl plus 5 moles of ethylene oxide has been studied[43] in chlorhexidine blends, against *S. aureus*. The time required to reduce viable counts by two log cycles, using chlorhexidine gluconate at 0·001% was reduced from 30 min, without any nonionic present, to 11·5 min blended with 0·0005% nonionic and to 2·5 min in the presence of 0·005% nonionic. Furthermore, the effect of these blends on cell suspensions revealed that this particular surfactant increases cell permeability, and an increased leakage of potassium ions was observed with equimolar concentrations of chlorhexidine and nonionic, thus supporting the view that increased penetration of chlorhexidine has resulted in membrane damage.

Table 4.15 Effect of 1% alcohol ethoxylate on chlorhexidine availability in an oil in water cream

Chlorhexidine gluconate concentration (%, w/w)	*Available chlorhexidine (%)*
0·10	7·2
0·37	14·6
0·73	19·4
1·00	19·5

It is often found that addition of a nonionic surfactant to a chlorhexidine formulation prevents precipitation of insoluble chlorhexidine salts from hard water or from formulations containing incompatible ions. Whereas a sorbitol ester is recommended[44] for the prevention of chlorhexidine chloride crystallisation from a contact lens cleaner formulation containing chlorhexidine gluconate in the presence of sodium chloride, this same surfactant can cause deactivation of cationic biocides when it is used as one of the inactivators in the biocidal test procedure (see Section 4.2.8). The level of nonionic surfactant in the solution is of critical importance. This is illustrated by measuring the percentage of available chlorhexidine in the presence of a nonionic surfactant, i.e. chlorhexidine which is not absorbed inside the micelles.[45] Table 4.15 shows the effect of a water-soluble alcohol ethoxylate on the deactivation of chlorhexidine gluconate in water.

Interactions between chlorhexidine and nonionics have been studied, using dialysis tubing to filter out the large molecular weight chlorhexidine–nonionic complex molecule.[46] In this way the complexed chlorhexidine was determined for different classes of nonionic, suggesting that with the more suitable surfactants, more than 50% and sometimes more than 70% of chlorhexidine remains uncomplexed and free to act as a biocide.

Three main types of surfactant were found to be suitable for mixing with chlorhexidine and these are listed below.

A. Alcohol–propylene oxide (PO)/EO condensates.
B. Ethylene diamine–PO/EO condensates.
C. Butylene oxide/EO condensates.

4.4.5 *Biocidal mechanisms*

The susceptibility of various organisms to chlorhexidine compounds is probably in the following descending order: vegetative bacteria, fungi and yeasts, fungal spores, bacterial spores. Its mode of action is probably similar in some respects to that of quaternary ammonium compounds. It is thought to absorb at the cell surface before penetrating to the cell membrane where it may inhibit membrane enzymes and promote leakage of cellular constituents. At higher concentrations the cytoplasmic constituents are in fact coagulated, reducing subsequent leakage of the contents. A discussion of some recent ideas concerning the mechanism of chlorhexidine attack on cells is discussed in Ref. 47. The possible effect of lipopolysaccharides working as a barrier to these biocides is explained. It is suggested that EDTA, which acts as a potentiator for quaternary ammonium compounds by increasing the permeability of this layer, does not work with chlorhexidine, therefore indicating some differences in mechanism. In discussing the action against Gram-negative bacteria it is suggested that the natural surfactants, the phospholipids, may assist the passage of chlorhexidine across the outer membrane. The action of chlorhexidine acetate against bacterial and fungal spores[48] suggest that this biocide inhibits spore outgrowth, but not spore germination.

4.4.6 *Practical applications*

In formulating chlorhexidine and its salts into useful practical products there are many pitfalls which have to be avoided. For example, chlorhexidine gluconate solution is affected by sunlight, and it is absorbed and therefore deactivated on cork and many other organic materials, so the choice of bottle stopper is important. Many of the problems associated with formulations arise from the insolubility of chlorhexidine salts, and Table 4.16 gives a selection of these values.[45] It is, therefore, apparent why chlorhexidine digluconate is the most common choice for aqueous based formulations. It is also obvious that formulations containing builders such as carbonates, phosphates and silicates will result in precipitates. Furthermore, the water supply used in making up formulations probably contains sufficient chloride or sulphate to form hazes. This is where the addition of suitable surfactants can overcome this problem without deactivating the

Table 4.16 Chlorhexidine salts: water solubilities at 20°C (%, w/v)

Diformate	1·0	Dihydrochloride	0·06
Diacetate	1·8	Dihydriodide	0·1
Dipropionate	0·4	Dinitrate	0·03
Malonate	0·02	Sulphate	0·01
Succinate	0·02	Sulphite	0·02
Tartrate	0·1	Di-acid phosphate	0·03
Dilactate	1·0		
Digluconate	>70		
Diglucoheptonate	>70		
Diisethionate	>50		

biocide. The pH of the solution is also important. A value of 5·5 is preferred for giving good biocidal activity at a pH which is acceptable to the skin. At pH 8 the chlorhexidine free base will precipitate and hydrolysis will begin to form *p*-chloraniline, an unwanted impurity. Some solvents will speed up the action of the chlorhexidine[49] and a solution in isopropyl alcohol is often used in hospital practice, although an emollient is necessary to avoid harsh skin reaction.

Various emollients used in cosmetic formulations have been examined together with chlorhexidine[50] and it is claimed that polyoxyethylene glyceryl monococoate, diisopropyl adipate, diisobutyl adipate and polyglycerol enhanced the bactericidal activity, particularly against *S. aureus*. The use of an emollient such as glycerol is common in teat dip formulations. Although the bactericidal effect can be reduced by including glycerol–nonionic combinations, the products are still sufficiently powerful to be effective. In fact, chlorhexidine is increasingly popular in this area, often preferred to alternative materials such as quaternary ammonium compounds or iodophors, for the following reasons:

(a) Chlorhexidine compounds are very mild to the skin.
(b) Chlorhexidine is nonstaining.
(c) Chlorhexidine does not taint the milk. Furthermore, traces of chlorhexidine which might get through to the milk are harmless, whereas traces of iodine are now considered to have undesirable effects, particularly on children.
(d) Iodophors are formulated with strong acids, e.g. phosphoric acid, and this can be particularly harsh to the skin, whereas chlorhexidine does not require the assistance of strong acids to be effective.
(e) Traces of quaternary ammonium compound which may carry through to the milk can cause problems with subsequent cheesemaking.

A very important area for the use of chlorhexidine based formulations is in hospital antiseptics. Surgical scrubs are formulated, using chlorhexidine gluconate with quite large quantities of surfactants, to produce a very effective biocidal detergent which must not be too harsh on the skin. A more general disinfectant used in hospitals and the home is based on a blend of chlorhexidine gluconate with cetrimide. This particular blend is considered to have a wide spectrum of kill plus reasonable detergency, supplied by the quaternary ammonium compound. Studies have shown that these detergent–biocide formulations are not only rapid in action against many types of bacteria, but the chlorhexidine adsorbs on the skin and its effectiveness persists for some time after application. This is of particular importance with surgical scrubs where the disinfected area must remain clean during the course of an operation. Furthermore, there are accumulative effects which show an enhanced biocidal efficiency building up after repeated washing.

4.4.7 *Formulations*

The following suggested formulations combine the biocidal effectiveness of chlorhexidine digluconate with the cleansing power of suitable, compatible surfactants. All percentages are expressed as active material.

(a) Surgical scrub[51]

Chlorhexidine digluconate	4%
Amine oxide	3·75%
Ethylene oxide–propylene oxide copolymer	25%
Water to	100%

(b) Antiseptic detergent concentrate

Cetrimide	15%
Chlorhexidine digluconate	1·5%
Isopropyl alcohol	10%
Water to	100%

(c) Teat dip formulation

Chlorhexidine digluconate	0·5%
Glycerol	5%
Nonionic surfactant	0·5%
Water to	100%

4.4.8 Biocidal testing

Test methods which are designed to imitate use conditions are often considered a good guide to the efficiency of detergent–biocide combinations. Chlorhexidine formulations are frequently used for skin washing preparations, in particular surgical scrubs. A test technique was first advocated by Price in 1938 and subsequently modified by Cade.[52] This consists of a standard washing of the hands and forearms a set number of times a day with the various antimicrobial detergents. Both transient bacteria, existing on the surface of the skin, and resident bacteria, which are much more difficult to remove from the pores of the skin, are collected in rinse basins. Five such basins would be used in any one test and the bacteria removed at each washing would be counted by some suitable technique. It is recommended that the test be carried out over the period of a minimum of 10 days, with perhaps 35 subjects, to give a good analysis of results. This method is recommended in the American FDA publication on topical, antimicrobial products.[53] Table 4.17 compares the effect of surgical scrubs containing chlorhexidine gluconate, hexachlorophene or an iodophor with a non-medicated piece of soap as a control. This hand washing experiment illustrates the superior effectiveness of the chlorhexidine formulation against the natural skin bacteria. Owing to the difficulty of organising such a large scale exercise, simpler techniques are sometimes used.

Table 4.17 Effectiveness of surgical scrubs against natural skin flora

Composition	*Survivors after 1 min wash (%)*	*Survivors after 5 × 1 min washes at 8 h intervals (%)*
Chlorhexidine digluconate (4%)	18·2	0·9
Hexachlorophene (3%)	35·5	10·0
Iodophor (0·75%)	20·5	5·9
Nonmedicated block soap	100·0	100·0

Source: N. Senior, *J. Soc. Cosmet. Chem.*, **24,** 259 (1973).

The method used in Ref. 54 tested the ability of the biocidal detergent to keep the hands of the surgeon free from bacteria during the course of an operation when the hand is covered with a surgical glove. Immediately after removing the glove, the finger and thumb pads of both hands are streaked in a regular pattern across agar plates containing a suitable inhibitor. The following three systems were compared by this method.

A. 4% chlorhexidine detergent;
B. 3% hexachlorophene detergent cream;
C. a povidone–iodine detergent.

Subsequent bacterial counts illustrated that the chlorhexidine based formulation was at least as good as the hexachlorophene version and better than the iodophor detergent in this particular test method. It is suggested that the fatty residues in the sweat are capable of inactivating iodine, which therefore fails to have the residual longer-term effect that the other detergents show. Washing with bar soap containing hexachlorophene was found to give the poorest results.

4.5 Phenols

4.5.1 General properties

Since the surgeon Lister introduced phenol into surgical practice in 1867 this group of compounds has been very widely used. Phenols are effective bactericides even against the tuberculosis bacteria. Many phenols are even better against fungi, but the virucidal and sporicidal properties are not particularly good. The efficiency varies with concentration to a very marked degree and it is in fact an exponential variation. For example, it is not unusual, on doubling the concentration of the phenol, to find that it kills the bacteria perhaps 50 times as fast. This effectiveness is, however, considerably reduced in the presence of even small amounts of organic matter. Compounds with many variations in structure are marketed as effective biocides. Substitution with C_6 or C_7 alkyl groups increases their effectiveness, but this increase is very selective according to the organism chosen. Introducing halogen atoms is another way of improving the molecule.

Various problems are associated with the use of phenolic compounds. They are rather insoluble in water; therefore, very careful formulating is required to solubilise the product into a usable form. This is normally done with anionic surfactants, which will be discussed in Section 4.5.2. Hexachlorophene was used extensively as a skin disinfectant for many years until in 1974 the US FDA published a report which indicated that the material could cause central nervous system disorder through its effect on the brain. Furthermore, it was suggested that its application to the skin in antiseptic formulations or in cosmetic creams could result in absorption through the skin with possible toxic effects.[55] Other phenolic compounds cause concern because of their toxicity and lack of biodegradability, e.g. pentachlorophenol is now banned in certain countries.

4.5.2 Anionic interactions

It is necessary to solubilise the phenol compounds with the aid of surfactants, and anionic surfactants have proved to be the most suitable type. At low soap concentrations, below the critical micelle concentration (CMC), the solubility of the phenol is very low, but above the CMC, solubility of the phenol increases rapidly as it dissolves within the micelle. It is thought to be the free phenol outside of these micelles which is the active biocide, capable of penetrating the bacteria cell wall. Originally, soaps such as potassium laurate, and other soaps of natural vegetable origin, proved to be successful. Unfortunately, these materials are susceptible to hard water and when the biocide is diluted the formulation becomes cloudy due to precipitation of calcium and magnesium soaps. Synthetic detergents do not, in fact, suffer from this problem and alkyl aryl sulphonates can be used successfully to formulate phenolic compounds. Although non-ionic surfactants deactivate phenols and therefore cannot be used (see Section 4.5.4), it has been found[56] that ethoxylated alcohols, which are then converted to the sulphate ester, are perfectly satisfactory materials for this purpose, provided that a low number of ethylene oxide groups is introduced. Figure 4.7 illustrates the effective dilution of parachlorometacresol (PCMC) when formulated with various molar ratios of the following surfactants.

A. Sodium alkyl phenoxy 8·5 polyethylene glycol sulphuric ester
B. Sodium alkyl phenoxy 17 polyethylene glycol sulphuric ester
C. Sodium alkyl phenoxy 30 polyethylene glycol sulphuric ester

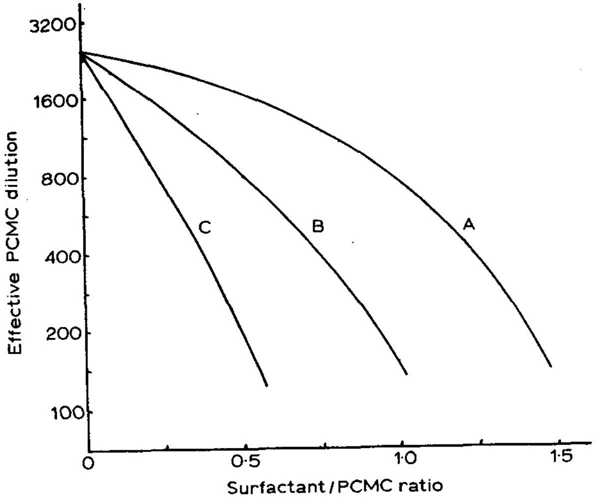
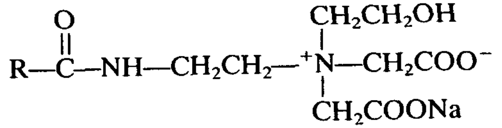


Fig. 4.7 Effectiveness of PCMC/surfactant blends versus *P. fluorescens*.

Sulphonated castor oil is a popular choice for solubilising phenolic materials, but it has been reported[57] that secondary alkane sulphonates are particularly effective in hard water.

4.5.3 Interactions with other nitrogen containing surfactants

Betaines are good detergents with a mild action on the skin and are therefore ideal for use in shampoos. They also act as good solubilising agents for phenols, and this blend can form the basis of medicated shampoos. The biocidal effectiveness of a combination of *p*-chloro-*m*-cresol with dodecylamine betaine was tested[58] against *S. aureus* and *P. fluorescens*. Figure 4.8 illustrates an increase in activity at first, as the betaine ratio increases, presumably due to the reduction of interfacial tension, followed by a fall in activity as the phenol is almost completely solubilised within the micelles. The following ampholyte structure[59]



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2CH_2{-}{}^{+}\underset{\underset{\displaystyle CH_2COONa}{|}}{\overset{\overset{\displaystyle CH_2CH_2OH}{|}}{N}}{-}CH_2COO^{-}$$

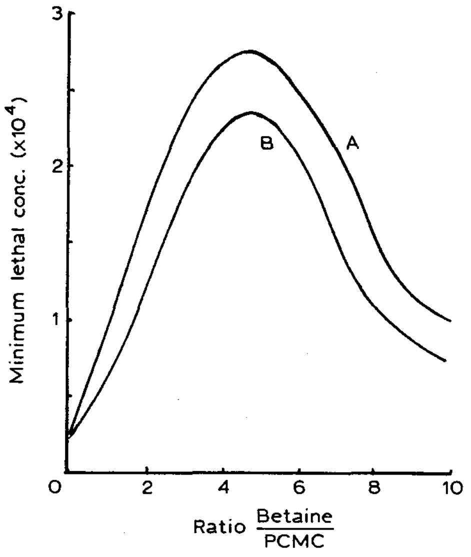


Fig. 4.8 Effect of a betaine on the biocidal activity of PCMC. A: *S. aureus*; B: *P. fluorescens*.

is also considered to be very compatible with phenols, and formulations using chlorinated bisphenol as the germicide are described.[60] This type of ampholyte is considered to give foaming stability together with excellent detergency and wetting properties without deactivating the phenol. It also has low toxicity with low skin irritancy.

Synergistic blends of quaternary ammonium compounds with phenolic compounds, in particular polyhydroxy diphenylmethane,[61] are sold to certain industries. Such a combination is claimed to control slime in the water used in papermaking, and this particular blend can also be added to the paper itself during manufacture to produce a sanitised product. Such a blend is self-emulsifiable in water and can therefore be easily used and dispersed. Synergism between a benzalkonium chloride and *m*-cresol was illustrated[62] by determining the fractional bactericidal concentration of the two preservatives to give specified sterilisation times against both Gram-negative and Gram-positive organisms. Figure 4.9 shows the result against *S. aureus*. Deviation from a single straight line is a measure of the synergistic effect. This is probably due to the lowering of the surface tension by the quaternary ammonium compound, thus assisting the permeation of the phenol into the cell membrane, its main site of action.

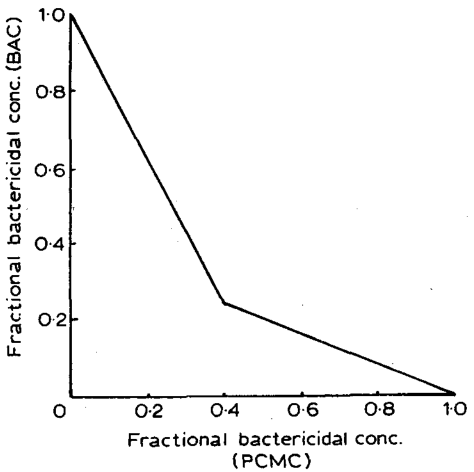


Fig. 4.9 Synergistic combination of BAC and PCMC.

4.5.4 *Nonionic interactions*

Generally speaking, relatively large concentrations of nonionic surfactants are likely to destroy the biocidal activity of phenols, by reducing the level of free phenol outside of the micelle to a very low value. However, it is claimed[60] that ethylene oxide/propylene oxide block copolymers are very effective solubilisers of chlorinated bisphenol, particularly when the ethylene oxide content is 40%. Furthermore, this type of surfactant has low toxicity, low irritancy and little taste, making it useful for formulations used in cleaning food contact surfaces. It has been shown that low concentrations of nonionic surfactant can improve the biocidal effect of phenolic compounds.[63] For example, the activity of phenol was determined in the presence of low concentrations of Polysorbate 80 on the bacteria *S. aureus*. Table 4.18 shows the results of such an experiment, illustrating clearly an increase in the biocidal activity at very low dilutions of nonionic below the CMC but a rapid decrease in activity as more nonionic is added, forming micelles and removing the phenol from the aqueous phase.

Table 4.18 Phenol–nonionic blends

Ratio of phenol : nonionic[a]	*Death rate of* S. aureus (*k/min*)
1:0	0·135
1:0·1	0·160
1:1·0	0·099
1:3·5	0·018
Phenol[a] + nonionic treated bacteria	0·267

[a] Phenol concentration: 0·64%.

Further results indicate that treatment of bacterial cells with a nonionic surfactant alone probably has a sublethal effect on the bacteria, possibly increasing the cell permeability and rendering the cell more sensitive to subsequent treatment with phenolic biocides. The last result in Table 4.18 illustrates this effect.

4.5.5 Biocidal mechanisms

It has been noticed that the activity of a series of phenol derivatives can often be related to the partition coefficient between oil and water, and more oil soluble derivatives being the most active. It is also observed that the acid form of the phenolic compound, which is the more hydrophobic form, is more active than the ionised form that is likely to occur in highly alkaline solutions. Therefore, it is likely that this lipophilic form of the phenol absorbs and penetrates the cell wall of the bacteria, affecting its permeability, possibly by reaction of hydroxyl groups of the phenol with the metal ions present in the cell wall. Increased permeability results in leakage of cell contents, presumably contributing to the lethal effect. Penetration of the phenol itself is thought to inactivate the essential enzyme systems. The beneficial effect of including chelating agents such as EDTA in phenolic formulations has been investigated[64,65] and it is likely that the EDTA again increases the permeability of the cell wall by reacting with magnesium or calcium ions which are present, therefore allowing better penetration of the biocide. Such a formulation is less effective in hard water because the beneficial effect of EDTA is lost by its combination with the ions in the water rather than those in the cell wall.

4.5.6 Practical applications

A good summary of the range of applications of phenolic compounds[66] includes the following areas:

- Wood preservation
- Water treatment
- Pulp and paper
- Leather
- Metal working fluid
- Cosmetics
- Adhesives
- Paint
- Textiles
- Disinfectants
- Antiseptics
- Surgical scrubs
- Toilet soaps
- Deodorants
- Pharmaceuticals

Leather preservation is an area where phenolic fungicides are particularly effective. A well formulated product will exhaust on the leather from an aqueous dispersion, particularly at the pickling or tanning stages. The wet skins often need protection for many months in hot climates, before being made up into leather goods. Figure 4.10 shows the uptake of a proprietary leather fungicide[67] indicating extensive exhaustion within the first 15 min of processing.

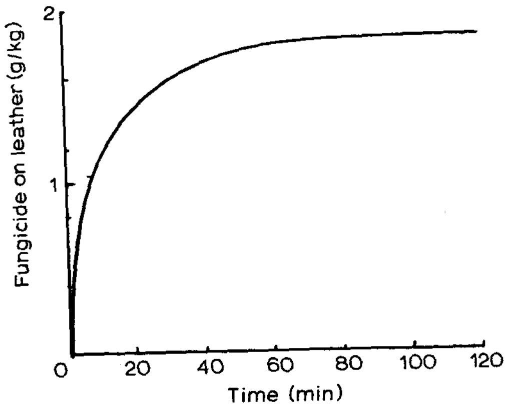


Fig. 4.10 Uptake of phenolic leather fungicide.

Properly formulated products, containing suitable surfactants, can give a durable surface cleaner in many other applications, whereas cleaners based on sodium hypochlorite are quick acting but much less durable. Early black disinfectants were based on coal tar products stabilised with soaps and the natural coal tar hydrocarbon neutral oils. In fact the neutral oils were found to have a synergistic effect against certain bacteria. In formulating phenolic biocides the pH is of some importance. In fact the insoluble acid form can often be dissolved by partial neutralisation with alkali to form the sodium phenate ion which, being water soluble, can solubilise the rest of the unchanged phenol, producing an effective biocidal solution. To give an example, 2,4,5-trichlorophenol, showing a phenol coefficient of 40, when tested at pH 6 against *Salmonella typhi,* only has a phenol coefficient of 1 at pH 10. It is possible to solubilise phenols in alkyl aryl sulphonates at pH values as low as 3 without precipitation problems. This would be impossible with a fatty acid soap.

4.5.7 *Formulations*

(a) Antiseptic/disinfectant—for home and hospital use (British Pharmacopoeia)

Chloroxylenol	5%
KOH	1·36%
Oleic acid	0·75%
Castor oil	6·3%
Terpineol	10%
Ethanol (96%)	20%
Water to	100%

(c) Disinfectant—for farm use against notifiable diseases[68]

Alkyl benzenesulphonic acid	15%
Glacial acetic acid	25%
High boiling tar acid	20%
Sodium xylenesulphonate	5%
Water to 100%	

(e) Surface cleaner[60]

Ethylene oxide/propylene oxide copolymer (40% EO)	15%
Ampholyte surfactant	10%
Chlorinated bisphenol	0·6%
Alkyl aryl sulphonate	5%
Sodium carbonate	2%
Water to	100%

(b) Antiseptic/detergent—boosted by including EDTA[65]

Dichlor m-xylenol	1%
EDTA	8·0%
Castor oil fatty acid	2·3%
Triethanolamine	17·3%
Terpineol	2·0%
Industrial methylated spirits	35·0%
Water to	100%

(d) Disinfectant—to dissolve in diesel or mineral oil for treating woodwork and animal houses. To emulsify in water as a general disinfectant[69]

High boiling tar acid	45%
Lauryl ethosulphate (60%)	5%
Oxitol	13%
Kerosene	35%
Sodium xylenesulphonate	2%

4.5.8 *Biocidal testing*

The Rideal Walker test goes back to 1903 and it determines the highest dilution of a disinfectant required to kill a specified organism within a set time interval under set conditions. In this method, phenol at 5% concentration is used as a reference disinfectant, and the phenol coefficient of the test product is determined, i.e. its activity compared to phenol. Many difficulties have arisen with regard to this test method. In the first place, the organism *Salmonella typhi* is difficult to use and is no longer considered to be the most relevant organism to test against. In the original test, water hardness was not considered and the presence of organic matter was ignored, yet phenols are now known to be deactivated considerably. The concentration effect is exponential, not linear, so it is, therefore, very difficult to extrapolate the results to various concentrations. Modifications to this method have been made over the years to reduce these objections. Hard water can be used and the test can include the presence of organic materials such as yeast extract or serum. *Staphylococcus aureus* is considered by many to be a more relevant organism for the test procedure. Comparing different types of disinfectant with phenol is not considered logical if the product being tested acts in a very different way from the phenol itself; for example, quaternary ammonium compounds are now tested by the British Standard method outlined in Section 4.2.8.

4.6 **Aldehydes**

4.6.1 *General properties*

The increasing use of heat sensitive materials in hospital instruments prompted the search for a chemical sterilising agent which could be used cold. An efficient sterilising agent has to be capable of destroying all forms of microbial life, including bacteria, fungi, tubercle bacilli and viruses. Such chemicals can be judged on their ability to kill the most difficult type, namely bacterial spores. Formaldehyde is capable of carrying out this task in 1 to 2% aqueous solution, but it does require a contact time of up to 20 h to destroy the spores. Furthermore, the fumes of formaldehyde are very irritating to the user and the chemical requires very efficient rinsing to avoid its toxic effects from upsetting the patient. In the early 1960s, glutaraldehyde was suggested as a possible alternative sporicide, as it is without these objectionable properties.[70] It is claimed that a 2% solution of glutaraldehyde, suitably activated with sodium bicarbonate will, at room temperature, disinfect within 10 min and sterilise within 10 h. Furthermore, it is surprisingly tolerant to the presence of organic matter such as serum, pus, etc.

The two most important factors affecting the general biocidal activity of glutaraldehyde are temperature and pH. As expected, its effectiveness will increase rapidly with temperature, but its most useful application is as a cold sterilising agent, and to achieve sufficient activity the pH is of great importance. Glutaraldehyde solutions at pH 7·3 or below are fairly stable on storage, but on the alkaline side the solutions are relatively unstable. For example, it has been estimated that at pH 8·5 the concentration falls from 2·1 to 1·3% over a period of 28 days at room temperature. It is, therefore, quite normal to sell glutaraldehyde solutions at an acidic pH, so these solutions need activating before use by adding sodium bicarbonate to bring the pH up to 8 or 8·5.

Formulations have been developed, often with the aid of surfactants, which either increase the biological activity of the stable acid solution or, alternatively, stabilise the biocidally active alkaline solution.

4.6.2 Anionic interactions

Increased stability has been achieved by the addition of 7% phenol in the form of a phenate buffer, holding the pH between 7 and 7·4. The life of an activated 2% glutaraldehyde solution was increased from 14 to 30 days.[71] In addition, it was shown that the sterilisation time against bacterial spores was reduced from 10 to 6·75 h. Furthermore, such a mixture has been granted Environmental Protection Agency (EPA) approval for use as a hospital disinfectant, below the normal 2% strength, so it does not stain the hands yellow. In addition to the phenol, an anionic surfactant used alone, or together with a nonionic surfactant,[72] increases the effectiveness of the formulation by assisting penetration to pores and crevices and irregular surfaces. Typical surfactants are sodium *n*-dodecyl benzenesulphonate and sodium cocoylsarcosinate. At higher levels of surfactant content, viz. 2–10%, an improved sporicidal activity is claimed. Several anionic surfactants such as dodecyl benzenesulphonate or dodecyl sulphate can be particularly effective when combined with divalent cations such as magnesium.[73] Therefore, magnesium salts of some organic acids increase the sporicidal activity of a 2% glutaraldehyde solution and at the same time extend the shelf life from a few days to several months, because in these formulations an acid pH can be maintained. It is also claimed that these stable acid glutaraldehyde solutions have a negligible reaction with organic matter, whereas the alkaline solutions can be deactivated. Table 4.19 illustrates the effectiveness of both the anionic surfactants and the magnesium ions, and Table 4.20 illustrates the excellent storage stability that can be achieved.

Table 4.19 Glutaraldehyde (2%, w/v) sporicidal activity

Additive	*Concentration (%)*	*Formulation pH*	*Viable spores[a] after 2h contact (%)*
None	—	3·6	30·0
Dodecyl benzene sodium sulphonate (DBSS)	0·25	4·18	1·0
DBSS + Mg^{2+}	0·25	3·82	0·08
Dodecyl sodium sulphate (DSS)	2·5	3·56	1·0
DSS + Mg^{2+}	2·5	2·76	0·1

[a] *B. subtilis*, initially 10^8/ml.

Table 4.20 Glutaraldehyde (2%, w/v) storage stability

Additive	*Concentration*	*pH*	*Time (min) for 99·9% kill[a] (formulation stored for weeks)*		
			0	4	52
None	—	3·6	>300	>300	>300
$NaHCO_3$	0·3%	7·9	40	>300	>300
$MgCl_2$	0·2M	3·5	120	120	125
Mg dodecyl sulphate (26·5%)	10%	4·5	55	55	60

[a] *B. subtilis* spores: 10^8/ml.

4.6.3 Interactions with other nitrogen containing surfactants

Aldehydes, particularly glutaraldehyde, have been used for some time in the oil industry to avoid bacterial contamination in drilling fluids and also to avoid contamination of the rock strata. To kill a wide range of organisms including sulphate reducing bacteria, quaternary ammonium compounds are sometimes blended with the aldehyde. In addition to improving stability of the aldehyde solution the surfactant properties of the quaternary ammonium compound may assist in its penetration, particularly when in contact with the slimes which often cover and protect colonies of bacteria. Glutaraldehyde alone has been found to be ineffective at disrupting this protective slime[75] and it may in fact stabilise it by some crosslinking action.

A blend of formaldehyde, glyoxal and glutaraldehyde can be used as a very efficient disinfecting agent in closed circuit toilets such as are found on aircraft, yachts, trailers, etc. These compositions must not attack aluminium alloys, and it has been found that addition of a quaternary ammonium compound avoids corrosive effects. Compounds such as alkyl trimethylammonium chloride are suitable materials.[76]

A fast-acting disinfectant with a wide range of bactericidal and sporicidal activity is made by blending glutaraldehyde with an alkyl betaine,[77] e.g. 2 g of dodecylalanine in 98 g of 25% glutaraldehyde solution. After adjusting the pH to 7·5 to 8 with 0·3 g of sodium carbonate, this disinfectant was found to compare favourably with sodium hypochlorite. The choice of surfactant in this case was influenced by its stability over a wide pH range, good solubility in water, good biodegradability and very low toxicity.

A definite synergistic effect has been observed[74] with as little as 0·1% of quaternary ammonium compound such as diisobutyl phenoxy ethoxy ethyl dimethyl benzylammonium chloride in a 2% glutaraldehyde solution. Spores of *Bacillus subtilis* (Method AOAC 1961) were killed in less than half an hour, whereas a 2% glutaraldehyde solution alone required a period of 3 h. Many other quaternary ammonium compounds are claimed to have this beneficial effect, particularly in the pH range 5–8.

4.6.4 *Nonionic interactions*

Some interesting work[78] shows the improvements that can be obtained by using glutaraldehyde in the presence of nonionic surfactants, while at the same time exposing the solution to ultrasonic irradiation. This investigation used dried spores of the very resistant *B. subtilis* with a 2% glutaraldehyde solution under a variety of conditions. Using ultrasonic radiation in a solution at pH 5, i.e. a stable pH, containing a nonionic surfactant such as an isomeric linear alcohol ethoxylate at a level of 0·2%, the minimum time for a 100% kill was reduced from 30 to 10 min. It is suggested that this effect of both the surfactant and the ultrasonic radiation is connected with the outer layers of the bacterial spore. Perhaps the radiation disrupts and depolymerises the polymer lattice in the murein which is present in the walls of all bacteria. The surfactant may then assist penetration of the glutaraldehyde into the damaged structure, increasing the absorption of the glutaraldehyde on to the reactive sites of the bacteria surface, resulting in a more powerful effect.

Table 4.21 Glutaraldehyde (2%, w/v) synergised with linear alcohol ethoxylate blend

Additive	*Viable spores*[a] (*10 tests*) *according to contact time*		
	16 *h*	18 *h*	20 *h*
Control	10/10	10/10	10/10
None	10/10	2/10	0/10
Rosin ester (0·25%) + 15 EO	10/10	2/10	0/10
C_{11-16} alcohol (0·25%) + 9–13 EO	0/10	0/10	0/10

[b] *B. subtilis.*

Work by the same author has been reported,[79] claiming that a 2% glutaraldehyde solution with a 0·25% mixture of nonionic ethoxylates from isomeric linear alcohols, has an increased shelf life, for example, 18 months at room temperature compared with only 6 months for unstabilised material. Even at 60°C it can be stored for at least 60 days. Table 4.21 shows clearly the synergistic effect of this type of nonionic surfactant against *B. subtilis* spores (vacuum dried).

4.6.5 *Biocidal mechanisms*

Since the effect of pH is so important, the structure of glutaraldehyde in acid and alkaline conditions has been studied. In acid conditions the molecule exists in the acetal form, so the aldehyde groups are reduced in number and the activity is low. In alkaline conditions free aldehyde groups exist but, in time, aldol polymers are formed which reduces their number. It appears that the aldehyde groups react with bacterial protein molecules to form complex crosslinking through the amine groups and this is more likely to happen in alkaline conditions. The effect is to seal the outer cell envelope preventing transport of material in or out of the cell. This can rapidly inhibit the cell's function, e.g. production of RNA, DNA and protein material. If glutaraldehyde makes contact with enzymes in the outer layers of the cell then presumably these also will be deactivated. Compounds such as sodium bicarbonate, which are used as activating agents, not only create the optimum pH for the aldehyde structure, but these materials also affect the cell wall and they appear to remove loosely bound outer layers of the cell, enabling the glutaraldehyde to penetrate further.

4.6.6 *Practical applications and formulations*

Glutaraldehyde was originally developed as a cold sterilising agent, particularly for surgical instruments.

Sterilising agent 1[80]

Activator—sodium bicarbonate	0·3 part
Surfactant,	
Corrosion inhibitor,	
Water to	92 parts
Glutaraldehyde (25%)	8 parts

Hospital steriliser 2[72]

Phenol	7·5%
Sodium phenate	0·20%
Sodium borate	2·35%
Diethylene glycol	6·30%
Sodium dodecyl benzene sulphonate (80%)	
Sodium dodecyl benzene sulphonate (80%)	7·00%
Sodium cocoylsarcosinate (30%)	10·95%
Water + hydrochloric acid to	92%
Glutaraldehyde (25%)	8%

Aircraft toilet disinfectant[76]

Formaldehyde	12·9%
Glyoxal	0·4%
Glutaraldehyde	6·75%
Dodecyl trimethyl ammonium chloride	3·00%
Nonyl phenol + 8EO	1·9%
Dye, perfume and water to	100%

4.7 The halogens

4.7.1 *General properties*

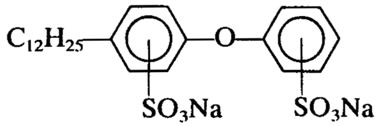
Chlorine, in the form of chlorinated lime, was already recognised as a useful deodorising agent in hospitals and in sewage treatment by the mid-19th century. Similarly, iodine is a well established disinfectant, and a tincture of iodine was used as long ago as 1839 for treating wounds. The principal objections to iodine as a skin disinfectant are its irritant and painful action and its staining of skin and fabrics. Furthermore, it is very corrosive to metals. These objections were largely overcome by the development of the iodophors, involving the use of surfactants to dissolve the iodine as explained in later parts of this section. The halogens have an excellent kill spectrum and have received wide approval for use in many applications. They can, however, be unsafe if not handled properly and they can be inactivated by alkali or by organic material. Chlorine is very susceptible to this problem. Hypochlorites are unstable in acid, liberating chlorine below pH 5, whereas iodophors are usually formulated with phosphoric acid present to increase the biocidal effect. The halogens are effective against vegetative bacteria, spore-forming bacteria, viruses and fungi. Algae are only controlled by chlorine, iodine being relatively ineffective and therefore unsuitable for use in swimming pools. Resistance to the halogen, of course, varies with the type of organism and *E. coli* is often used as a test species because it is a more resistant vegetative bacterium than many other types.

4.7.2 *Anionic interactions*

To assist the cleaning power of sodium hypochlorite solution it is desirable to add a surfactant to increase penetration and wetting. First of all the surfactant must be stable to the powerful oxidising action of the hypochlorite, and one patent[81] describes a suitable biodegradable-isodecyl alcohol sulphate with good hard water resistance. If low foam is an important factor then the sodium salt of an alkyl ether carboxylate of the following type is preferred.[82]

$$C_8H_{17}O(C_2H_4O)_nCH_2COONa \qquad n = 1\text{–}10$$

Stain removal from greasy surfaces such as table tops, again requires the assistance of a good detergent, and a formulation adjusted to pH 11 with various alkaline builders in the presence of alkyl sulphate and sodium dodecyl diphenyl oxide disulphonate is recommended.[83]



A similar surfactant is used to formulate an iodine based detergent[84] where liberated iodine is solubilised in the presence of 2-methoxyethanol and some phosphoric acid. Such solutions are claimed to be stable for 1 to 2 years, still retaining 90%, or more, of the original available iodine. A phosphate ester can be used to prepare an iodine sanitiser[85] particularly suitable for automated or continuous-line bottle washing, where low foam and quick draining is required. In this case a C_{10-14} alcohol is ethoxylated with less than 5 moles of ethylene oxide before phosphating and neutralisation with triethanolamine.

Iodine could not normally be incorporated into a soap bar because it would react with the fatty acid, particularly with unsaturated parts of the molecule. However, it has been reported[86] that detergent bars can be made from the synthetic coconut acid ester of sodium isothionate:

$$\text{coco}—COOCH_2CH_2SO_3Na$$

This solid surfactant has a low inorganic salt content and can be moulded into bars with good foaming and lathering properties even in hard water. Apparently a polyvinyl pyrrolidone–iodine complex can be added during manufacture to produce a product showing strong germicidal activity against various bacteria, yeasts and fungi. Furthermore, the eye irritation of this material is not worse than that of conventional soap, and it does not stain fabrics.

4.7.3 *Interactions with other nitrogen containing surfactants*

Hypochlorite based disinfectants have been improved by making the liquid thicker so that it clings to vertical surfaces such as toilet bowls, sinks, baths and other areas of use. This increases the contact time and therefore improves biocidal efficiency. Unfortunately, the normal polymer thickening agents are attacked by the hypochlorite and are

quite unsuitable for this particular application. However, amine oxides and certain betaines, in conjunction with anionic surfactants, have proved to be very effective thickeners. The anionic component is usually a soap, an alkyl sulphate or, most probably, an alkyl ether sulphate. Good thickening can be achieved with less than 3% of surfactant, and the ratio of amine oxide to anionic material has a large effect on the viscosity achieved. Saturated soaps are effective, in particular sodium laurate.[87] Amine oxides and betaines also solubilise suitable bleach stable perfumes, particularly blends of terpene, hydrocarbons, camphor, cineole and linalool. Furthermore, the thickening produced by these surfactants stabilises the dispersion of a chlorine stable pigment, Ultramarine Blue.[88] An alternative type of anionic surfactant[89] can be used in combination with amine oxides or betaines, namely sodium alkyl sarcosinates

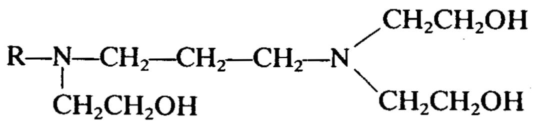
$$CH_3(CH_2)_{11}CON(CH_3)—CH_2—COONa$$

or alkali metal taurides, e.g.

$$\text{Alkyl}—CON(CH_3)—CH_2CH_2SO_3Na$$

Good viscosity, stability and a steady available chlorine level are observed after storage for several weeks at temperatures up to 37°C.

Quaternary ammonium compounds are capable of solubilising iodine, but as an antiseptic solution it could prove too irritant to the skin and to membranes. However, ethoxylated fatty quaternaries are claimed[90] to improve the stability of iodophors by reducing loss of iodine due to vaporisation and prolonging the activity, when tested by the method of Cantor and Shelanski. Stabilisation with quaternary ammonium derivatives of fatty diamines



has also been claimed,[91,92] particularly when acidified with phosphoric acid.

A cold sterilisation method is desirable in hospitals and operating theatres, demanding a biocide that will kill spores within 15 to 30 min at room temperature. Chlorine dioxide alone is not sufficiently active in this respect, but it has been found[93] that a 1:1 combination with certain types of quaternary ammonium compound produces the desired increase in kill rate. The normal single chain alkyl benzyl dimethylammonium chlorides are not effective but dialkyl quaternaries, in particular didecyl dimethylammonium chloride, are claimed to be very efficient improvers.

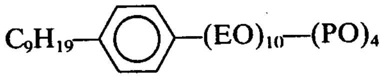
4.7.4 Nonionic interactions

The usefulness of iodine as an effective biocide was enormously improved by dissolving in nonionic surfactants to produce iodophors, a much cleaner and less irritant form. Their advantages are listed below.[94]

(a) They permit the application of iodine in a safe and convenient way.
(b) They are almost odourless.
(c) They are almost nonirritant and nonsensitising.
(d) Their toxicity is very low.
(e) They have good detergency from the presence of the nonionic surfactant.
(f) Germicidal activity of the iodine is unaffected, e.g. it is almost equally powerful against all vegetative types of bacteria.
(g) Iodine is effective over a wide pH range. It can be used at a much lower pH than hypochlorite, which evolves chlorine below pH 5.
(h) Iodophors have low temperature coefficients, i.e. they are still very active at cold temperatures.
(i) Although all sterilising agents are affected by organic matter, iodine is less affected than chlorine or quaternary ammonium compounds.
(j) Organisms tend not to develop resistance to iodine.
(k) Iodophors are stable when stored.

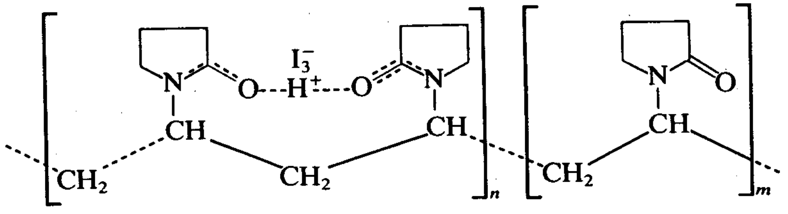
Iodophors can be made containing from 0·5% available iodine up to perhaps 20% available iodine. This can be achieved by dissolving the iodine in a water soluble alkyl phenol ethoxylate containing over 60% of ethylene oxide. It has been found advisable to acidify with phosphoric acid to obtain the maximum biocidal efficiency. Typical ratios of nonionic surfactant to iodine vary from 3:1 to 10:1 and it is found that a small part of the iodine remains bound to the surfactant, so perhaps only 80% of the total iodine is titratable and effective as a biocide.

Another particularly effective, less foamy, type of surfactant for dissolving up to 20% iodine, is a water soluble ethylene oxide/propylene oxide block copolymer.[95] Alternatively, a relatively low foaming iodophor can be made from an alkyl phenol ethoxylate blocked with a number of propylene oxide groups.[92] For example



Foam is important because iodophors are often used in the cleaning of food preparation plants where they are circulated under pressure, producing foam which is difficult to rinse away, and giving rise to residual iodophors being left in the food product, e.g. milk. Apart from affecting taste, an undesirable health risk exists, particularly to small children.

Perhaps the best known iodophor is that which is made by dissolving iodine in a polymer based on 1-vinyl-2-pyrrolidinone.[96] This makes a stable, reddish brown powder which is water soluble, non-irritant and non-staining. It is used in hospitals for preoperative skin disinfection and for the prevention and treatment of infections in wounds, ulcers and burns. There is little evidence that povidone–iodine is significantly inactivated by the presence of organic matter. An investigation of this product under model clinical conditions[97] illustrates a rapid and uniform bactericidal effect against bacterial pathogens. Spectroscopic investigations have shown that the povidone–iodine structure contains not molecular iodine (I_2) but hydrotriiodic acid (HI_3) as shown below.[98]



$m = 18n$

Special surfactants may be incorporated into iodophor based teat dips to prevent teat sores and cracks caused by the solubilising nonionic surfactant. These emollients must be of a type which do not reduce the level of available iodine but in fact help to solubilise the iodine. It is necessary to add 75 moles of ethylene oxide to make lanolin water soluble for this purpose, but unfortunately this reduces its emollient properties. However, it is claimed[99] that lanolin plus 5 to 15 moles of ethylene oxide is quite suitable provided that water soluble synthetic C_9–C_{11} alcohol ethoxylates are also incorporated into the product, which is then acidified with phosphoric acid to increase the stability.

Bromine is also recognised as a very reactive bactericide and it is possible to make bromophors[100] by adding liquid bromine to a liquid nonionic surfactant in a ratio of about 1:2.

4.7.5 Biocidal mechanisms

In a chlorine based disinfectant the biologically effective chlorine can exist in three forms, namely molecular chlorine (Cl_2), hypochlorous acid (HOCl) and as a hypochlorite ion (OCl^-). The relative amounts of these three species are largely governed by the pH of the solution and the following equilibria are established:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

$$OCl^- + H_2O \rightleftharpoons OH^- + HOCl$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

It is recognised that the hypochlorous acid molecule is the most potent biocide and its concentration is obviously dependent on pH. The hypochlorite ion does contribute to the biocidal effect but is thought to be only 1/80 as effective as the acid form. Figure 4.11 illustrates the importance of pH in determining the concentration of the effective hypochlorous acid.

The details of how the hypochlorous acid actually attacks the microorganism has never been worked out thoroughly, although several theories exist. For example, chlorine is known to react with amine groups to form chloramines and this may happen with the proteins in cell membranes, thus interfering with cell metabolism. Alternatively, such modification of the cell membrane may allow diffusion of the cell contents out of the cell or, in fact, it may disrupt the cell membrane altogether. Other workers have suggested that the very low chlorine level required for bactericidal effect indicates that the reaction must be with some vital enzymes within the cell itself. Reaction with such enzymes may, in fact, be with the SH group of cysteine in the protein or with amine groups to form *N*-chloro compounds. Other workers have suggested that some oxidising reaction is the vital mechanism for initial attack on microorganisms, and an outline of these various theories is given in Ref. 101.

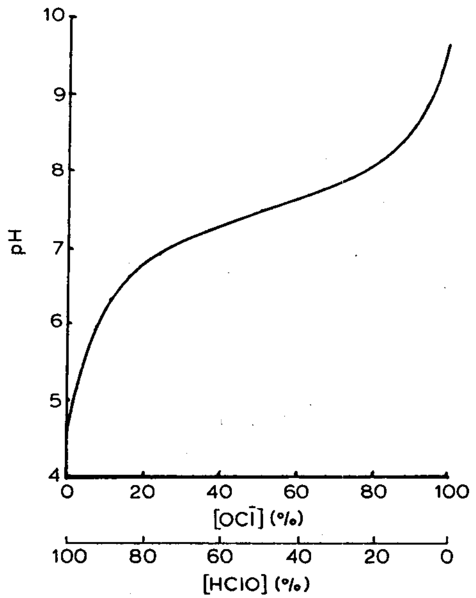


Fig. 4.11 Effect of pH on hypochlorite composition.

It has been found that various types of organism exhibit resistance to hypochlorite depending on the conditions of use. Such resistance can usually be overcome by increasing the concentration or temperature or by changing the pH. Among the bacteria, *E. coli* is generally more resistant than other vegetative bacteria and it is a useful test organism for evaluating the disinfecting action of chlorine based disinfectants. Spore-forming organisms can be considerably more resistant and it has been suggested[102] that in such spores the molecular configuration of the protein protects the SH group of essential enzymes from attack by the chlorine.

Iodine disinfectants are subject to the following equilibrium reactions in aqueous solution:

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^-$$

$$HOI \rightleftharpoons H^+ + OI^-$$

$$3I_2 + 3H_2O \rightleftharpoons IO_3^- + 5I^- + 6H^+$$

$$I_2 + I^- \rightleftharpoons I_3^-$$

Calculations show that at pH values less than 9 the iodine exists almost entirely as molecular iodine (I_2) plus hypohalous acid (HOI) and in fact iodine disinfectants do not have the same sharp dependence on pH as the chlorine based examples. In fact, from the calculations the following conclusions can be drawn.

(a) Reducing the pH below 6, i.e. making the iodine disinfectant acidic, reduces the formation of the relatively inactive iodate ion (IO_3^-).

(b) Above pH 7, the formation of inactive iodate increases, but this can be counteracted by adding more iodide ion in the form of sodium iodide which drives the equilibrium the other way in favour of iodine formation.

Disinfectants based on iodine are therefore preferably used on the acid side but they still exhibit reasonable effects under weak alkaline conditions, perhaps up to pH 9. Iodine in its molecular form is thought to penetrate the cell wall of microorganisms quite rapidly, but the exact method of killing cells is not known for certain. It may be assumed that the basic NH groups in proteins and in nucleic acid groups will be changed, which in turn will disrupt the hydrogen bonding. Groups such as SH in the amino acid residues like cysteine will also be changed and this will prevent some crosslinking. Furthermore, any amino acid residue containing a phenolic group is likely to be substituted by the very bulky iodine atom, causing steric hindrance problems. Unsaturated carbon–carbon double bonds will react with iodine causing changes in the lipid components of the cell.

In iodophors the iodine is thought to be dissolved in the micellar aggregates of the surfactant carrier, therefore iodine as I_2 or HOI is greatly reduced in the aqueous phase. The objectionable properties of unpleasant odour, irritation, staining and metal corrosion are therefore absent. As the iodophor is diluted the micelles will break down, therefore releasing free iodine to act as a germicide. In fact, less free iodine is available in a concentrated iodophor solution than in a more dilute form and it passes through a maximum value as shown in Fig. 4.12. In the case of povidone–iodine solutions this maximum occurs at about 0·1% concentration.

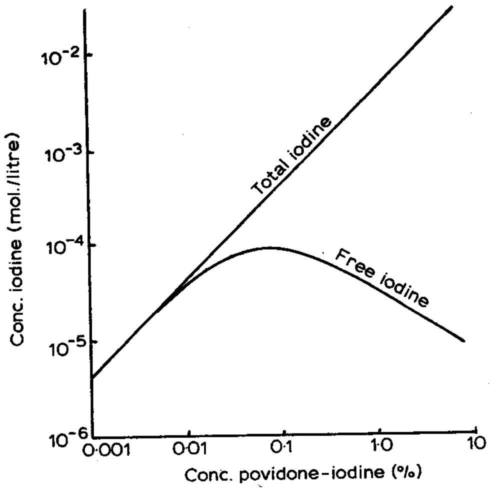


Fig. 4.12 Available free iodine in povidone–iodine solutions

4.7.6 *Practical applications*

In many applications chlorine disinfectants may come in contact with organic material, e.g. milk residues in dairy cleaning. Whereas sugars and starches do not seem to affect the germicidal activity of chlorine, protein residues can reduce the biocidal activity. The chlorine will react with amine groups to form chloramines which may, in fact, be bactericidal but their action is much slower. On the other hand, water hardness does not have a very significant effect on the action of chlorine, so this is a definite advantage. Iodophors are not so affected by the presence of organic matter so they make excellent antiseptics in the presence of blood and serum. Chlorine based disinfectants in the form of hypochlorites are widely used in the household, hospitals and public buildings. They are used in restaurants and other food processing areas such as dairies, canneries, breweries and beverage bottling plants. In addition, they are used for treating drinking water, swimming pool water and all types of waste water effluents. Iodophors may be used in some of these applications, e.g. in the food processing industry, dairies and bottling plants. Perhaps their most important use, however, is in the hospital field where they are used as surgical scrubs and in general preoperative preparations for the skin. They can also be used for therapeutic purposes, e.g. in the treatment of infected and burned skin, where iodophors have largely replaced aqueous and alcoholic iodine preparations because of their less irritant nature. Iodophors can also be used in the hospital for disinfecting equipment, provided that it does not undergo any discolouring reaction with the iodine.

The MAFF has published a list[103] of available teat dips based on iodophors containing emollients such as glycerine, sorbitol or lanolin derivatives with three strengths of iodine, namely 0·5% for direct use or 1·5% or 2% stock solutions for further dilution. Iodophors are also mentioned in the American FDA publication, part 178, Indirect Food Additives: Adjuvants, Production Aids, and Sanitizers. Up to 25 ppm of iodine is allowed for cleaning food contact equipment, utensils and surfaces, and approved surfactants are listed for the formation of iodophors. Hypochlorites are also approved for this purpose up to a level of 200 ppm available chlorine. Detergents and sterilants used in the brewing industry are discussed in Ref. 104, where it is emphasised that the conditions for using hypochlorite based disinfection have to be chosen carefully, bearing in mind the following important points.

(a) Hypochlorite cannot be formulated in acid conditions because it liberates dangerous chlorine gas.
(b) The concentration of the effective hypochlorous acid decreases as the pH is raised.
(c) Corrosion of stainless steel is reduced as the pH is raised.
(d) Biocidal activity is synergised by the presence of hydroxyl ions (OH^-) at pH values of 11 to 12.

4.7.7 *Formulations*

Simple iodophor[105]	
Iodine	1 part
Alcohol	9 parts
Complex ethylene oxide/propylene oxide block copolymer	10 parts
Water	80 parts

Germicidal detergent bar[86]	
Polyvinyl pyrrolidone–iodine	5–20%
Coconut acid ester of sodium isothionate	15–25%
Cetyl alcohol	0·5–3%
Polyethylene glycol 4000	65–75%

Iodophor sanitising cleaner[84]	
Dodecyl diphenyl oxide disulphonate (50%)	64·6%
Potassium iodide	4·7%
Sodium bromate	0·7%
2-Methoxy ethanol	20%
Phosphoric acid (85%)	10%

Teat dip iodophor[106]	
Alcohol PO/EO condensate	5%
Linear alcohol ethoxylate	5%
Glycerol	3%
Phosphoric acid (88%)	1%
Iodine	2%

Biodegradable teat dip iodophor[99]	
Lanolin alcohol + 5EO	3%
Iodine	2·5%
C_9–C_{11} alcohol + 6EO	5%
C_9–C_{11} alcohol + 12EO	5%
Phosphoric acid (80%)	0·7%
Water	83·8%

Thickened bleach[87]	
Coco alkyl betaine	0·72%
Sodium laurate	0·28%
Perfume	0·08%
Caustic soda	0·05%
Sodium hypochlorite (15%)	66·6%
Water	100%

Thickened bleach[89]	
Sodium hypochlorite (to give 5% available chlorine in total composition)	96·6%
Sodium hydroxide	0·4%
Sodium lauryl sarcosinate (30%)	1·0%
Myristyl amine oxide (30%)	2·0%

4.7.8 *Biocidal testing*

Several chapters of the book by Seymour S. Block entitled *Disinfection, Sterilisation and Preservation,* 3rd edn, 1983,[101] are devoted to the numerous methods devised for the testing of disinfectants of all types. Ideally, the test method should reflect very closely the realistic use conditions. The efficiency of iodophor germicides compared to various other types has been evaluated,[107] using a handwashing technique. Basically, two tests were involved; one attempts to measure the reduction in natural microorganisms already present on the hands, whereas a second test inoculates the hands with two relevant bacteria before attempting to kill them, namely *E. coli,* a possible enteric pathogen in food, and *P. fluorescens,* representing potential spoilage bacteria. In these experiments a uniform handwashing exercise was performed with exactly 15 s exposure time to the disinfectant, followed by standard rinsing of the hands. Rinsing with plain tap water and rinsing with a nongermicidal soap were carried out for comparison purposes. Table 4.22 illustrates some of the results of a prolonged test over many days, illustrating the superior efficiency of the iodophor

Table 4.22 Efficiency of germicidal handwashing agents

Agent	*Count reduction (%)*	
	E. coli	P. fluorescens
Tap water	78·4	71·3
Control soap	96·3	96·5
Chlorhexidine (4%)	98·9	99·1
Chlorhexidine (2%)	97·0	97·1
Iodophor (0·75%)	99·2	99·5
Iodophor (0·3%)	97·5	97·4

containing 0·75% iodine and the chlorhexidine based product containing 4% chlorhexidine.

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5 Defoaming agents

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5.1 Introduction

Although the title chosen for this paper is defoaming agents it could easily have been entitled antifoam agents, foam inhibitors, foam suppressants, foam control agents, deaerators or even air release agents. In fact, all these names describe, in one way or another, the means by which foam is controlled by the use of chemical surfactants.

The very fact that there are so many names describing the function of foam control is indicative of the mystique surrounding this very important class of surfactants and how, even at this time, so little is known about the theory of foam control and the means available for controlling it.

All these terms are widely used within the many separate industries in which foam is a problem. They are often used interchangeably and this often creates confusion. In reality, for example, the most widely used terms, antifoam and defoamers, are interchangeable. However, they can describe quite separate functions.

An antifoam, for example, as the word implies, is a product that prevents the formation of foam. A defoamer, on the other hand, is a product that will cause an existing foam to break. Commercial defoamers and antifoams, if they are at all viable, will both break existing foams and prevent further foam formation, thereby combining both functions. However, some defoamers, quite simply, can only act in breaking foams and are quite unable to act as antifoams. In fact, once the solute has become saturated with these defoamers, the product ceases to even act as a defoamer. Examples of this type of product are short chain alcohols and, in general, these have very limited use commercially.

While the act of defoaming is by far the most dramatic function of a foam control agent, prevention of foam formation is generally the most economical and practicable way of solving foaming problems. In fact, the author would prefer to promote the usage of the word antifoam because this describes the bulk of the action of these products and the most economical way they should be used. However, the term defoamers is very widely used and will, in all likelihood, be used for many years yet.

5.2 The problem of foam

Although foam is mainly a 20th-century problem, the containment of foam has probably been a problem for many centuries. The problem then was mainly contained within the kitchen, and many a cook (even nowadays) knew that a dash of butter or fat added to the pan will prevent the contents of the pan from boiling over. There is one reference to a manufacturer in the last century using a leg of pork suspended over his processing tank to contain the foaming produced during manufacture. This is probably the first recorded reference to the use of fatty acids in the pork as a defoamer!

While there are many industries in which foam is used to great advantage, such as in ore flotation, fire-fighting foams, etc., in many industries it is a considerable problem. Foaming can lead to poor utilisation of plant, pump cavitation, uneven dyeing of textiles, and fire hazards in distillation processes. In fact, the problem touches many industries and produces a great diversity of associated problems.

5.3 The theory of foaming and defoaming

5.3.1 *Theory of foaming*

To understand how and why defoamers work one has to understand what makes a stable foam. Pure liquids are unable to sustain a stable foam and this can be explained thermodynamically.[1] For a one-component system that has sufficient surface area to make the surface energy a significant contribution to the total energy, the change in free energy is given by the Gibbs equation:

$$dG = V\,dP - S\,dT - \gamma\,dA \qquad (5.1)$$

where γ is the surface tension of the liquid and where A is the surface area per mole. Hence

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P.T.} \qquad (5.2)$$

Integrating eqn (5.2) gives

$$\Delta G = \gamma\,\Delta A \qquad (5.3)$$

where ΔG is the change of free energy at constant temperature and pressure.

If eqns (5.1)–(5.3) are applied to a foam, a decrease in the Gibbs function results from a decrease in area which, of course, can be affected by coalescence of the foam. Hence, foam composed of pure liquid is thermodynamically unstable and has only a momentary existence.

However, when, for example, water becomes contaminated with a surface active solute and is aerated, a foam is produced, and surfactant molecules transfer from the bulk to the greatly expanded new surfaces. An energy balance is produced in the foam as any decrease in surface area lowers the free energy in the system and this is balanced by an increase in free energy caused by the transfer of the surfactant molecules from the surface back into the bulk of the system. This has the effect of introducing some stability to the foam. One should point out at this stage that all foams are thermodynamically unstable and will be reduced, sooner or later, to the preferred state of bulk liquid with minimum surface area, i.e. totally free from foam.

Experience has shown that the presence of a surfactant alone is not enough to ensure stability against the action of gravity and other stresses which can destroy the foam. It is generally agreed that other contributory factors help sustain the life of the foam.

Drainage of liquid from the foam walls under gravity reduces film thickness and makes the foam more fragile. Drainage is reduced by high bulk and surface viscosity. Evaporation also reduces foam stability, so that components with low volatility can improve foam stability. The use of glycerol in children's bubble blowing kits as a foam stabiliser is well known as it retards both drainage and evaporation of soap films.

The formation of gelatinous surface layers enhances the stability of foam. Protein polysaccharide complexes are adsorbed at the bubble surfaces in beer foams, immobilising the fluid by creating a high resistance to flow.[2] Film elasticity is often a major factor in foam stabilisation. Rupture of a bubble wall is thought to start with a localised thinning spot. As this spot stretches, the local surfactant concentration decreases, thereby increasing the surface tension in the thinning area. An inward force directed towards the centre of the thinned area occurs and liquid from the surrounding surface is drawn towards the spot. Underlying layers of liquid are drawn with it, preventing further thinning at the weak point. This is called the Marangoni effect.

If the surfactant concentration is restored quickly by migration of the surfactant molecules from the bulk before repair of the thinning spot occurs, the bubble will break. However, most surfactant molecules migrate relatively slowly to the surface and, in general, are unable to prevent the film elasticity effect prevailing.

Other means by which foams are thought to be stabilised include electrical double layer repulsion, reduction of gas diffusion between bubbles and entropic double layer repulsion. However, in general, surface elasticity and surface viscosity are probably the two most important factors affecting the stability of most troublesome industrial foams.

5.3.2 *Theory of defoaming*

The majority of chemical defoamers are liquids which are insoluble in the foaming medium. If they were soluble they would, being surface active, almost certainly promote foam. These liquids must not only be insoluble in the foaming medium but current thinking states that the liquid must also spontaneously enter the bubble and spread across it, causing the bubble to rupture. To achieve this they must have a positive entering coefficient (E) and spreading coefficient (S) expressed as follows:

$$E = \gamma F + \gamma FA - \gamma A \tag{5.4}$$

$$S = \gamma F - \gamma FA - \gamma A \tag{5.5}$$

where γF and γA refer to the surface tensions of the foaming medium and defoamer, respectively, and γFA is the interfacial tension between them.

What is thought to happen is that the defoaming liquid displaces the foam stabilising surface active agents from the foam's surface and prevents the Marangoni effect of film elasticity healing any potential film rupture. At the same time the defoamer liquid, by displacing the foam stabiliser, will probably speed up the rate of drainage, thereby reducing the stabilising effect of surface viscosity.

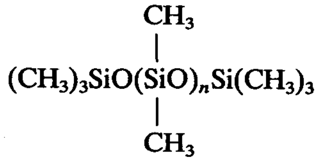
The theory, in itself, does not explain the need for hydrophobic particles suspended in many of these liquid defoamers. Without these hydrophobic particles many of the defoamers would be largely ineffective. Some researchers claim that these hydrophobic particles act as defoamers by a dewetting process, which results in the spontaneous withdrawal of the foaming medium immediately surrounding the particle on the surface of the bubble, resulting in its rupture. In these cases, the liquid element of the defoamer has been described as merely a carrier for the solid particle, although the carrier should have, one supposes, sufficiently low surface tension for the product to have a positive entering and spreading coefficient. Certainly, the nature of these hydrophobic particles is extremely important but their presence is not always necessary as there are many cases of very effective liquid defoamers whose performance is not enhanced by addition of these solid particles. Therefore, the author feels that there is much more research work to be carried out before we fully understand the theory of defoaming.

5.4 Composition and types of defoamers

Defoamers can be split into two main categories, silicone based and organic defoamers. Although the silicone based and organic defoamers are quite different chemically, both categories work by displacing the foam stabiliser from the air–liquid interface. We need to examine both categories.

5.4.1 Silicone defoamers

As a class, silicone defoamers are generally regarded as closest to attaining the mantle of 'universal defoamer'. They combine two properties rarely found together, namely involatility and low surface tension. Also, they are chemically inert and are insoluble in water and in many organic systems. Their chemical inertness makes them relatively nontoxic to both man and the environment. Traditional silicone antifoams are based on combinations of polydimethylsiloxane fluids



$$(CH_3)_3SiO(\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}O)_nSi(CH_3)_3$$

and hydrophobic silica (SiO_2), without which they would have very little defoaming activity, particularly in water based foaming systems.

The traditional silicone antifoams are generally supplied as oil-in-water emulsions for use in water based foaming problems. For nonaqueous foaming problems, the 100% active compounded silicones or even the pure silicone fluids are the recommended products. In these nonaqueous applications it is vital that the silicone used is insoluble in the foaming system. Should solubility occur, the silicone, being highly surface active, will exacerbate the foaming problem rather than relieve it!

In general terms, silicone antifoams are at their best when prevention of foam for the duration of a process is needed under conditions of high shear and high levels of low surface tension surfactants. However, it is probably their extreme versatility and acceptability over a wide variety of conditions that has made them particularly acceptable to industry. This, combined with the fact that the defoaming technology is continually moving forward with the advent of new silicone polymers, should keep silicones in the forefront of industrial defoamers for many years to come.

5.4.2 Composition of silicone defoamers

The preparation of silicone defoamers, even today, is still more of an art than a science. However, by combining art with science, consistent and effective defoamers can be produced by those companies that have the equipment and technical capabilities to do this.

In the case of silicone defoamer emulsions, their defoaming/antifoaming performance will depend on various parameters including emulsion particle size, surfactants used, activated silica used and method of emulsification.

With regard to emulsion particle size, it has been found that particle sizes of diameters less than 2 μm contribute very little to antifoam performance. This is believed to be due to the silicone being too easily assimilated into the bulk liquid and not able to orientate at the air–liquid interface. Also, there is some evidence that, at low particle sizes, the dispersed silicones can become solubilised in any surfactant micelles that are present.

On the other hand, particle sizes in excess of 50 μm, while giving good 'knock down' of stable foam, can easily 'oil out' when added to a foaming system, resulting in poor long-term antifoam efficiency and potential spotting problems in, e.g. textile dyeing applications.

Therefore, one needs to aim at attaining particle sizes of between 2 to 50 μm when making silicone defoamer emulsions and this is achieved by a combination of using the correct emulsification equipment and choice of surfactants. A combination of a low hydrophilic lypophilic balance (HLB) surfactant such as glyceryl monostearate, with a high HLB surfactant such as polyethylene glycol monostearate, is commonly used. These surfactants are themselves low foaming and minimise the possibility of overemulsifying the silicone antifoam compound, resulting in poor defoaming/antifoaming performance.

In the last decade or so, some of the more exotic silicones have been increasingly used, such as copolymers of polydimethylsiloxane and poly(alkylene oxides), generally known as silicone glycols. By varying the ratio of silicone to glycol and the molecular weights of both, all sorts of permutations can be obtained with varying effects on their defoaming performance. Fluorinated silicones have also been increasingly used as a result of their insolubility in a wide variety of solvents. However, their very high cost has limited their general acceptability. Another trend has been to combine silicones with organic defoamers, combining the advantages of both types of defoamers and thereby producing a synergistic effect.

In conclusion, silicone defoamers rarely fail to control a foaming problem. However, they are not always the preferred product as their cost effectiveness in certain industries is inferior to the organic based defoamers. Also, there can be undesirable side-effects from their use, such as 'fish eyes' in surface coatings, which make them unacceptable. However, the technology is being developed to eliminate these side-effects from silicones and this is going to widen the scope of silicone defoamers in the years ahead.

5.4.3 Organic defoamers

This category covers a multitude of different chemicals, both formulated and single chemical products. This is partly due to the fact that so many organic surfactants exhibit defoaming properties to a lesser or greater degree and partly because, in general, they tend to be specific in action, and a formulated product developed for one specific application will not necessarily show much activity in other applications.

Generally speaking, the organic defoamers are at their most cost effective in systems incorporating low concentrations of relatively mild surfactants being operated under low shear conditions. Some of the most serious industrial foaming problems incorporate such foaming conditions, and many very excellent organic defoamers have been developed to control these problems effectively and most economically.

5.4.4 Composition of organic defoamers

As has already been mentioned, organic defoamers can either be single chemical or formulated products. To illustrate the diversity and range of organic defoamers, the following is a list of types of organic defoamers currently in use in industry: aluminium soaps of stearic or oleic acid; polypropylene glycols (mol. wt >2000); copolymers of polypropylene and polyethylene glycols; fatty acids and their glycerides and/or ethoxylates; higher alkyl alcohols, e.g. *n*-octyl alcohol, cetyl alcohol; dispersions in mineral oil of high melting point waxes and/or hydrophobic silica (sometimes a surfactant is added to aid dispersion); tributyl phosphate; fatty amides dispersed in a liquid hydrocarbon carrier. These products may be supplied as ready to use liquids. They can also be supplied as powders and solids, which require predispersion in water before they can be used. Also, they may be supplied as either oil-in-water or water-in-oil emulsions.

5.4.5 Summary of desirable chemical and physical defoamer properties

The most desirable properties of a defoamer will vary depending on the particular application in which it is to be used. However, in general terms, the following properties are likely to be the most important considerations in choosing a defoamer: lower surface tension than the foaming medium; insoluble in the foaming medium and resistant to solubilisation and/or degradation by the foaming medium; positive spreading coefficient to allow it to spread on the air–liquid interface; nontoxic to both man and the environment; low BOD, COD and TOD values; easy to handle; stable on storage particularly at extremes of temperature; produce an economical solution to the foaming problem; good foam knock down and subsequent foam control; free from undesirable side-effects.

5.5 Foam problems by industry and the defoamers used in controlling them

5.5.1 Textile industry

For many years, the ability of a soap to produce a stable foam was indicative of its quality. That is, the more foam a soap was able to produce, the better was its detergency. With increasing mechanisation and extra demands placed on the classical soaps, these soaps have been gradually replaced by more efficient surfactants.

A surfactant alone does not produce the problem of foam. In textile finishing, foam can only be produced in combination with mechanical influences such as the incorporation of air into the finishing system either by the textile material itself or by mechanical processes.

The increase in textile production that has occurred over the years has resulted in an increasing foam problem in the industry. New finishing machines, incorporating higher rates of liquor circulation through the goods, denser winding of bobbins, shorter treatment times and the use of shorter liquor ratios have all exacerbated the foam problem.

At the same time, the quality of the goods has to be continually improved which, in part, means that the foam problem has to be controlled without loss of quality of the finished product.

The problem of foam in textile finishing can manifest itself in many ways: flotation of textile goods resulting in unlevel dyeing, poor liquor uptake in padding processes, channelling in package dyeing, bursting in wound packages, cavitation in pumps leading to pump failure, staining of dyed goods resulting from deposits of dye foam, and interference with measuring and metering devices.

All textile finishers use defoamers to a lesser or greater extent. The defoamers used, particularly in dyeing, are predominantly silicone based as these are recognised within the industry as being the most efficient defoamers.

These silicone based defoamers are generally oil-in-water emulsions and can vary in silicone strength from 5 to 30%. The more popular strengths are 5 and 10%, which allows the defoamer to be added directly without a great risk of overdosing and excessive defoamer losses due to wastage.

The better quality emulsions are formulated such that the silicone particle sizes are controlled within certain limits, 5–50 μm, to give an emulsion combining good dyebath stability with good defoaming/antifoaming performance. Achieving a satisfactory defoamer for textile processes needs great care in formulation and manufacture. For a defoamer to be effective, there must be a high degree of instability, so that a dyebath defoamer has to achieve this fine balance between good stability and good foam control.

In the early days of introducing silicone defoamers into the textile industry, the importance of dyebath stability was not recognised. Many cases of oil spotting were recorded because of the silicone oiling out under the high shear and temperature conditions in the dyebath. Gradually, the major defoamer suppliers and the textile industry itself, by a combination of improved defoamer formulations, more knowledge of how best to use the defoamers and good housekeeping, thereby not allowing silicone deposits to accumulate in the dyebath, have largely overcome the instability problems with silicones.

The most cost effective and safest way of adding defoamers to textile finishing operations, and this principle applies to the use of defoamers in most applications, is to add it on a continuous or semicontinuous basis. This will prevent foam becoming a problem and will reduce the chances of spotting. Certainly prevention is easier than cure when dealing with foam problems and this principle should be adhered to whenever possible.

It is not always possible, however, to add defoamers in this manner, and the advent of jet dyeing some years ago was a process where shear and temperature conditions were particularly harsh, but the defoamers could only be put into the machine at the start of the operation. The defoamer would have to be able to control foaming throughout the jet dyeing process yet remain stable. Some of the traditional silicone emulsions ran into serious trouble in these machines and the defoamer industry set about producing more stable products.

Defoamers based on copolymers of polydimethylsiloxane and poly(alkylene oxides) were developed which combined good defoaming performance with good stability. Of course, these only worked if they were insoluble. This meant that the foam problem had to be at a temperature in excess of their cloud point. Unfortunately, at high surfactant levels in the dyebath, the defoamers' cloud point was sometimes raised to a level in excess of the dyebath temperature and they ceased to control foam.

Currently, the successful defoamers used in jet dyeing are a combination of much improved but conventional type silicone emulsions, the silicone glycol variety of defoamers and products combining both types of defoamers.

A recent development in defoamers for the textile industry is the advent of the 'sinker' defoamers. Removal of entrained air from hanks in carpet dyeing has always been a problem. If this is not successfully achieved, the hanks tend to float, thereby preventing level dyeing. Some conventional silicone defoamers were partially successful in sinking the hanks whereas others had no effect on this problem at all. Silicone based defoamers are now available that are extremely successful in both removing this entrained air and, at the same time, control surface foaming in the dyebath. These same products are also showing great potential as penetrating agents and possibly an entirely new market is being opened up for these 'sinker' defoamers.

5.5.2 Fermentation industry

Many industrial fermentation industries encounter serious foaming problems during production. The foam is often proteinaceous in nature and, in these cases, the foam is thought to be stabilised by the absorption of the proteins in the gas/liquid interface and then subsequently denatured.

For fermentation processes, foam presents many hazards including contamination and blockage of the sterile exit filters, enrichment of cells and their autolysis in the foam. There is also, of course, the loss of production capacity due to the foam having to be accommodated in the production vessel and, in extreme cases, the contents have been known to siphon completely out of the vessel. This is particularly costly when excise duty has already been paid on the contents as in the case of beer brewing!

The fermentation based industries in which foam is a serious production problem include the following: antibiotics; enzymes; yeasts; single cell protein; wine, beer and spirits; some organic acids, e.g. citric, vinegar; and industrial alcohol.

As one can see, the fermentation industries which encounter serious foaming problems are quite diverse and often their individual requirements for defoamers are quite different, even within each individual sector. Many types of defoamers are used in these processes. The ones most commonly used in fermentation processes are as follows.

5.5.2.1 Alcohols Although the higher alcohols (>8 carbon atoms) are still used to a limited extent in the fermentation industry, they are largely dated. Octyl alcohol was one of the earliest defoamers used in this industry.

5.5.2.2 Natural oils and fats These have been used for many years and are still used in large quantities, particularly in antibiotics and enzyme manufacture. Their disadvantages are that their batch-to-batch defoaming performance is often variable. Also, as they are often used as combined nutrients/defoamers, an oil or fat with good nutritional properties does not always have the best defoaming properties and vice versa. Therefore, at the end of a fermentation process, one can be left with a large excess of oil or fat that has been added in excess of the nutritional requirements and which, presumably, was the excess needed for defoaming.

Chemically, these oils and fats are glycerides, esters of glycerol with long chain saturated or unsaturated monobasic acids, together with some free fatty acid. The most common oils and fats used as defoamers are soya bean oil, ground-nut oil, olive oil and lard oil. Sometimes they are used as carriers for a more effective defoamer such as a silicone.

5.5.2.3 Polyethers These are commonly used in the fermentation industry and are polymers and copolymers of ethylene oxide and propylene oxide. These polymers and copolymers must be insoluble in water to be effective defoamers, so the polyethylene glycols, which are water soluble, are not used as such. The most common polyether type defoamer used in this industry is polypropylene glycol of mol. wt *c.* 2000. More recently, combinations of polyether type products combined with silicones have proved very effective defoamers in some fermentation processes.

5.5.2.4 Silicones Silicone based defoamers, both in the emulsified form and as 100% active compounds, are used extensively in these processes. In many fermentation processes, before the defoamer can be applied, it has to be sterilised, generally by heating the product under pressure for up to 3 h at 125° to 140°C. For water based emulsion type products this sterilisation process can very easily break the emulsion. Emulsion type silicone defoamers are now available which are stable to these sterilisation processes. Some of these sterilisation stable products become almost gel like at high temperatures and this stabilises the disperse phase. A more recent development has been to protect these emulsions without the need to produce this gel-like structure and this makes handling the product much easier.

There are a number of features required in a defoamer for fermentation processes, some common to general foaming problems, some unique to fermentation processes. These are as follows:

General properties Good foam knock down; high antifoaming activity at low concentration; good cost/efficiency performance; non-toxic, odourless and tasteless; readily dispersible in the foaming system.

Unique properties Nontoxic to the microorganisms being produced; nonmetabolisable; no effect on oxygen transfer; does not interfere with subsequent processing; withstands heat sterilisation.

Several of the desirable unique properties of defoamers need further explanation. The requirement of the defoamer being non-metabolisable is, perhaps, a little controversial as, e.g. natural oils and fats, which are generally metabolisable, are used extensively in some fermentation processes. However, there have been reported cases where the end products of the metabolisation process can seriously alter the fermentation process. Therefore, there is a case for using a nonmetabolisable antifoam, whenever possible, as this removes one element which can interfere significantly with the fermentation process thereby making a very complex process a little less complex.

Another property is the effect of the defoamer on oxygen transfer. This is a very complex phenomenon which is dependent on the degree of aeration and agitation, viscosity, microorganism concentration and morphology, contact time and the surface parameters of the system. Several studies have been made on the effect of defoamers on oxygen transfer. Sometimes the evidence has been that defoamers have adversely affected oxygen transfer and in some cases, the oxygen transfer has been improved. More work needs to be done in this area but it is clear that the defoamer used can make a significant impact on oxygen transfer and consequently the defoamer can have a great effect on the yield of microorganism, either adversely or beneficially.

The importance of the effect of the defoamer on subsequent purification procedures is sometimes ignored. Two very important (membrane) processes, which are becoming increasingly important in downstream processing of biologically active proteins from microbial sources, are ultrafiltration and crossflow filtration.

At present, the major problem in applying these techniques for harvesting and separation of microbial cells from spent media is the rapid fouling of the membranes during their operation. One type of agent contributing to this problem is the defoamers. Being essentially hydrophobic and insoluble, defoamers naturally tend to absorb or coat on to the membrane surface.

A recent study has shown that, out of the several types of defoamers tested, polyglycols have the greatest fouling effect and silicone emulsion has the least effect.[3] Reducing the particle size of the defoamer is one way to reduce the fouling problem although there are limits to this because, if the particle size is reduced to too low a level, the defoamer will lose its defoaming activity. Membrane fouling is an important and growing problem and further investigation of this is clearly required.

In conclusion, the fermentation industries present very special and often complex foaming problems. The defoamer producing industries have not put enough development work into this area, but this is understandable in view of the very complex nature of the problems and the difficulty of reproducing the problem in the laboratory. Greater cooperation between the fermentation and defoamer producer industries will be required before significant progress in resolving the associated problems of using defoamers in this industry are attained.

5.5.3 Food industry

The food industry is probably one of the oldest industries that has lived with the problem of foam and has effectively controlled foaming by the use of defoamers. With the modernisation of food processes, foam has become a much more serious problem. This fact, combined with the tendency for food additives to come under the microscope, has meant that much more attention has been given to the defoaming requirements of this diverse industry.

Like the fermentation industry, foam is a problem common to many sectors of industries which are involved in the processing of food. To give some idea of those sectors which encounter the most serious foaming problems, a list of these is given: potato processing, evaporation and dehydration of foods, fruit drinks, instant coffee, soft drinks, pickle processing, sugar molasses, vegetable processing, sugar beet processing, liquid sugars manufacture, edible oil processing, dairy industry. This list is not comprehensive as there are many other parts of the food industry which still encounter, albeit less serious, foaming problems.

Uncontrolled foam in the food industry can be a source of the following problems:

(a) Severe loss of production capacity.
(b) Inefficient mixing and pumping.
(c) Down time losses due to cleaning foam clogged lines and filters.
(d) Product wastage due to foam overflow.
(e) Spillage hazards.
(f) Cleaning problems due to foam overflow.

By the careful selection of a suitable defoamer, all of these problems can be either overcome or considerably reduced at minimum cost. Of course, the choice of defoamer is somewhat limited in this industry because of the regulations governing the use of defoamers in foodstuffs. Not only must the defoamer meet the prevailing regulations of the country in which it is used, but also, if the food is exported, the defoamer may well have to meet the regulations of the country to which it is exported. In general, therefore, food grade defoamers must meet the following requirements:

(a) High performance, thereby reducing addition levels to a minimum.
(b) Be either nontoxic or, at the very minimum, have a low order of toxicity.
(c) Comply with food regulations.
(d) Odourless and tasteless.

These are in addition, of course, to the general requirements of being easy to handle, biodegradable and either sterile or sterilisable.

As has already been stated, the choice of defoamers available for the food industry is somewhat limited due to the need for the products both to have a low order of toxicity and be permitted by the prevailing regulations of the country in which it is to be used. However, in general, the following types of defoamers are used in food industries in the West.

5.5.3.1 Mineral oil/animal fat combinations These types of product were used extensively in certain industries such as sugar beet processing. They were cheap, but not very efficient. Generally, they were only used in those industries where the end food product (e.g. white sugar), after processing, was either totally or almost totally free from contamination by the defoamer. Their use as defoamers is rather less popular these days because mineral oil is not an acceptable food additive in many countries.

5.5.3.2 Polypropylene glycol/silicone mixtures This type of product is increasingly used for certain food processes such as the sugar beet industry.

5.5.3.3 Fatty acid ester/alkoxane ethers of fatty alcohol combinations These are used in a variety of food processes including potato processing and the sugar beet industry.

5.5.3.4 Silicones A variety of silicone (polydimethylsiloxane) based defoamers are used in the food industry. They are permitted for use in foodstuffs in many countries, including, e.g. the UK, USA and FRG. Sometimes they are permitted, but only for certain foodstuffs. The products are available in oil-in-water emulsions and compounded form. The emulsions are available in concentrated (50% active) down to ready to use (5–10% active) forms.

5.5.3.5 Vegetable oil based Vegetable oils, both the purified form and activated in emulsion form, are used extensively in the food industry. They are used in, e.g. potato crisp manufacture and whey processing.

As food regulations become more and more stringent, it is possible, in the years ahead, that only two basic groups of defoamers will be fully approved for food. These are edible glyceride and polydimethylsiloxane based products. Should this occur, greater effort will have to be made to ensure that the performance of these products will cope with the multiplicity of foaming problems within the food industry. Also, it will mean that the food industry, which is often quite conservative, will be forced to look for alternative defoamers to the traditional products used for generations, and this may result in their finding more effective and versatile products for their processes.

5.5.4 Surface coating industries

Foam can be a serious problem in many surface coating industries. For example, the problem of foaming in water based paints is mainly incurred during the pigment stage of paint manufacture. The air that is entrapped within the pigment is displaced as wetting occurs and becomes entrapped in the mill base. Also, of course, air is drawn into the process during mixing and milling. This can also occur with water based printing inks and with solvent based paints and inks.

Failure to incorporate a defoamer into the surface coating system can lead to a variety of problems such as follows:

(a) Loss of production capacity.
(b) Difficulty in filling containers because of air entrainment.
(c) Following on from (b), the slow release of entrained air on storage may result in loss of volume in container, giving the appearance of 'short measure'.

(d) Foam problems during application of both paints and inks resulting in surface defects such as 'fish eyes' (protruding unburst bubbles) or craters resulting from burst bubbles. Fish eyes and craters affect the visual appearance of the surface coating and can have an adverse effect on its protective function.

Therefore, selection of an appropriate defoamer before making the surface coating, is, in almost all cases, an absolute necessity.

Unfortunately, as in all other industries, any defoamer that is going to be effective has to be incompatible with the medium it is being used to defoam. This, of course, introduces a new factor into this equation as the defoamer must effectively reduce or eliminate foaming/air entrainment without causing surface defects in the surface coating. Therefore, the acceptable defoamer has to achieve this fine balance between sufficient incompatibility in order to be an effective defoamer, but sufficient compatibility to prevent producing the same defects as is produced by the foaming/entrained air.

The selection of the appropriate defoamer is absolutely critical and either silicone or nonsilicone based defoamers can be considered these days. Traditionally, nonsilicone based defoamers have dominated this particular sector of industry. This is probably because when silicone antifoams were first introduced some 30 years ago, every industry, including the surface coating industries, took them on board with great eagerness. Unfortunately, by a combination of overzealousness of the suppliers to sell them, poor stability of the silicone antifoams and lack of caution in using them by the industry, some disastrous results were obtained.

The silicones defoamed the system very well but the poor stability of the products at that time introduced serious surface defects. It reached such a point, at one stage, that many paint manufacturers would not allow any silicone based product near their plant and who could blame them. These days, the silicone based antifoams are often much more stable and consistent products and this, combined with the availability of more compatible second generation silicones, such as silicone glycols, have made them much more acceptable defoamers for this industry.

On the nonsilicone defoamer side, there are many excellent defoamers available to the industry. The formulation of these products is not generally disclosed but they are often thought to consist of at least three ingredients as follows:

(a) Carrier—generally a mineral oil.
(b) Hydrophobe, and this can be microcrystalline wax or hydrophobic silica.
(c) Emulsifier—this ingredient is added to enable the defoamer to disperse in the foaming system.

Other additives are occasionally added, e.g. silicone, to give the defoamer extra bite!

Experience in the use of defoamers in surface coatings both helps the users and supplier in selecting the appropriate defoamer for a particular system. However, in most cases, extensive laboratory testing of defoamers takes place before deciding on a particular one.

These tests must simulate, as closely as possible, the foaming problem. They have to be carried out under reproducible conditions and generally consist of at least one, and possibly all, of the following tests:

(1) Tests on the finished surface coating. Agitation of the surface coating, under controlled conditions of agitation and temperature, containing different defoamers at different concentration levels. The amount of air/surface foam is assessed by weighing a set volume of product. The higher the weight of product, the lower the air content and consequently the better the performance of the defoamer.
(2) A defoaming test which determines the effectiveness of the defoamer in knocking down an existing foam. Once again, conditions must be controlled and be reproducible.

Both these tests simulate the manufacture of the paint or printing ink system. Tests should also reproduce the subsequent end use of the product, and in such tests the paint or printing ink, containing different defoamers, can be applied with a sponge or lambswool roller on to a substrate.

The film is allowed to dry and the surface checked for either the presence of fish eyes or craters from the foam or surface defects from the defoamer. Sometimes, it is difficult to differentiate if the defects are due to poor foam control or from the defoamer. However, the presence of the defects from whatever source is certainly going to eliminate *that* defoamer from being chosen.

Another important test that any defoamer must pass, particularly if the foaming problem is an end use one, and that is that they must retain their performance on storage. Defoamers after appearing very effective immediately after addition can lose performance either by being slowly solubilised in the system or by simply separating out of the system. Therefore, storing the surface coatings for 4 to 6 weeks at ambient or slightly above ambient temperature and retesting is absolutely critical. Many defoamers fail at this final hurdle.

In conclusion, while experience will assist the surface coating specialist to select the most suitable defoamer, he will still have to subject the defoamer to a variety of tests such as described before he can be sure that it is totally acceptable.

5.5.5 Pulp and paper manufacture

Both these manufacturing operations use prodigious quantities of defoamer, mainly organic based. Foam during pulp production is at its most serious during the washing process. Surface foaming at this stage, if not controlled, results in liquor spillages and fibre losses. Even the operators are at risk from injury in this situation. In such a situation, flow rates have to be immediately reduced, and more dilution water applied to get the foam under control. At the same time, of course, the resultant mess has to be cleaned up and the spilt liquor treated, thereby placing an extra BOD/COD load on the sewage plant. All these activities result in extra costs.

Of course, foaming during washing can be easily controlled by the use of an appropriate defoamer. The scenario we have described above is when either none or insufficient defoamer is applied during the process.

Fortunately, this particular aspect of washing foaming is relatively easy to cure. Surface foam, while being unsightly, is the least harmful to washing efficiency. One can react quickly to an increase in surface foaming by addition of extra defoamer. However, lack of surface foaming does not necessarily indicate that the washing process is taking place efficiently.

In addition to the surface foam there is generally a large volume of minute entrained air bubbles. These extremely small stable bubbles often attach themselves to the surface of the cellulose fibres and inhibit the drainage of the washing liquor through the fibre mat as it passes over the vacuum drum.

They also take up volume that could be filled by the fibre, thereby creating a lower density pulp on the drum than is desirable. The entrained air, because it inhibits drainage, results in more recoverable chemicals passing downstream with the fibres.

The defoamers used in the pulp washing process, therefore, must be able to cope with both the surface foam and the entrained air bubbles to maximise drainage of the mat on the vacuum drums. Some defoamers are more successful than others in this respect but the general feeling, both in pulp and paper manufacture where a similar entrained air problem exists, is that further improvements in removing this entrained air are desirable and the totally effective defoamer in this regard has yet to be developed!

The most successful defoamers used in pulp washing processes have been oil based defoamers (OBDs) consisting of combinations of mineral oil, fatty amides and hydrophobic silicas. However, by a combination of factors such as escalation in prices of petroleum based products and environmental pressures on mills to minimise the volume of chemicals that are introduced into the waste stream, new concepts in defoamers have been examined in recent years. The concept of water extended defoamers, which are water-in-oil emulsions, have been developed for this industry which, in addition to giving good foam control, claim to give less pitch formation, lower soda losses, improved drainage and reduced bleach demand, properties not easily attained with OBDs. In addition, the lower levels of hydrocarbons present in those defoamers, and ultimately in the mill effluent, will result in less BOD/COD pressure on the treatment plant.

Another type of defoamer increasingly used in the industry, which again is water based, is the gel type defoamer. This consists of gel particles dispersed in water, the gel particles being composed of, e.g. long chain fatty soaps, long chain fatty alcohols and water. The water is claimed to be an integral part of the defoamer particle, and the structure of the gel particle is likened to that of a liquid crystal.

The gel particle is very hydrophilic and will not penetrate an air/water interface. To do so, it must be hydrophobic and this occurs when it is added to a foaming system which contains high valency ions such as aluminium ions in an alumed rosin system. A hydrophobic shell of aluminium stearate is thus formed. After this hydrophobic shell has formed the gel particle can penetrate a film between two bubbles. The interior of this gel particle is extremely surface active and causes an 'explosion' of the gel particle into smaller particles at the surface. This causes a rupture of the films between the bubbles. These gel type defoamers have been available for many years in the form of a 'brick' or solid defoamer. The user generally had to make up the defoamer in his plant and in a very dilute form. Suppliers of these gel type defoamers can now provide them to at least 20% solids and as they do not involve the use of oils, waxes, silicas or solvents, they could have significant advantages over those defoamers that do.

All the above-mentioned defoamers are used extensively in the wet end of the paper making process. The cost of achieving foam control and deaeration is always going to be extremely important in this industry, but increasingly, environmental considerations are becoming more and more important. Therefore, the future development for defoamers in this industry will probably be to achieve the following criteria:

(a) Higher cost efficiency.
(b) Better performance, particularly with regard to deaeration.
(c) Improved ecological properties.
(d) Reduction in side-effects from defoamer such as pitch formation.

5.5.6 Water treatment—sewage and desalination

The treatment of water is a very large and diverse industry. It encompasses local authorities' sewage plants treating vast quantities of both domestic and industrial sewage to small sewage plants treating a company's industrial sewage before releasing it into the town's drains.

Outside Europe, particularly, where the climate is very hot and sources of potable water are very limited, there is a large industry producing potable water from seawater. These plants are generally called multistage flash (MSF) desalination units.

Foam is a problem common to all these plants and vast quantities of antifoam are applied to keep the various foaming problems under control. To discuss the problems associated with these two different operations, it is best to treat them separately.

5.5.6.1 Sewage treatment Foam can be a problem at any of the various stages of sewage treatment. Obviously, foaming tends to limit the capacity of the plant and this is costly. Also, foaming of effluent can be a hazard to both man and the environment. There have been many reported cases of uncontrolled foaming being blown across busy roads, and apart from the unsightly mess it creates, its presence can and has caused traffic accidents! If the foam contains untreated sewage, the foam could also be toxic. There is even a case where an operative on a sewage plant fell into one of the plant's aeration beds and because of the deep surface foam on these beds, he was not seen and subsequently drowned. Therefore, control of foam in sewage treatment is of great importance both to the industry and the environment, and, because of the great volumes of liquid to be treated, foam control is a very costly process operation.

The defoamers generally used in sewage treatment in the UK are hydrocarbon oil based. Sophisticated metering equipment is used to dispense the defoamers, at controlled flow rates, to all the points on the sewage plant where foam is a problem.

More expensive defoamers, such as silicone based defoamers, have not generally been used in this industry because of their high cost in relation to the much cheaper hydrocarbon based defoamers. However, where sophisticated metering equipment is available, which would enable much lower concentrations of defoamer to be added, there is some evidence that the more expensive and complex defoamers could be used without incurring extra cost.

In fact, legislation may well be the trigger for a complete rethink on defoaming problems in sewage treatment. In North America, it is the general practice to chlorinate all sewage treatment before final discharge after treatment. Residual hydrocarbons in the effluent can be chlorinated by this treatment, the end products of which are toxic to fish. In Canada, the use of these hydrocarbon based defoamers is banned. In the USA, these defoamers are not banned provided they do not produce any restricted compounds, such as chlorinated hydrocarbons, in the discharged effluent. The net result is that the use of these hydrocarbon based defoamers is limited in the USA.

In the UK, effluent is not chlorinated so the risk of producing chlorinated hydrocarbons when using hydrocarbon based defoamers is minimal. However, as pressures to use more environmentally acceptable chemicals increase perhaps we may see a move in the years ahead to alternative defoamers in this industry.

5.5.6.2 Desalination Excessive foam in MSF desalination plants can give rise to salt contaminated distillate and reduced operating efficiency. Plant operating variations in pressure, temperature, flow and seawater feed composition and alkalinity can perturb vapour/liquid equilibria, resulting in increased levels of foam. Since the foam cannot always be controlled by mechanical means, defoamers are, in the main, used to control foaming in these plants.

In addition to controlling foam, a defoamer must not interfere with heat transfer or with the performance of the scale control additive. Neither must the defoamer contain steam-volatile components that can contaminate the distillate. It also must be stable at MSF operating temperatures and residence times and it should be compatible with the antiscalant feed solution.

Seawater, of course, is not a pure liquid. In addition to 3 to 4% of inorganic salts, it often contains traces of organic matter that have surface active properties. The actual process in the MSF plant produces the foaming conditions, and the trace seawater impurities stabilise it.

Foam is initiated during the explosive decompression of superheated brine in the first stages of the plant. Massive volumes of CO_2 and water vapour are evolved from the turbulent liquid. If the CO_2 venting capacity and/or water condensing capacity of the stage are inadequate, stage pressure will increase, slowing gas diffusion, thereby stabilising foam and reducing water production. In the lower temperature stages of a plant, higher salt content and lower temperature of the brine increases surface viscosity which also stabilises foam. Foaming also occurs occasionally in mechanical deaerator sections.

The relative importance of these factors varies among MSF plants throughout the world. Most plants have a potential foaming problem and sometimes the problem is very serious. However, the correct use of an appropriate defoamer will generally restore efficient plant operation.

Defoamers that are used in MSF plants are often of the polyethylene glycol monoalkyl ether type which generally fulfil the various criteria for defoamers for MSF plants. Silicone based defoamers are also used with some success although there is still a body of opinion that considers they could reduce heat transfer by depositing and crosslinking on the heat exchangers during their use. As far as the author knows there is no actual practical evidence of this.

5.5.7 Petroleum processing

Defoamers are used extensively in the petroleum processing industry. As the majority of foaming problems in this industry are involved with nonaqueous systems, the great majority of defoamers used, and in some cases the only defoamers that are effective, are silicone based. The main foaming problems associated with petroleum processing are as follows:

5.5.7.1 Gas/oil separation This is the largest single foaming problem within the petroleum processing industry, and silicones are recognised by the industry as the only successful means of controlling it. Crude oil from the well contains dissolved gas that has to be removed. During the removal of the gas, severe foaming problems often occur.

Silicone fluids, of different molecular weights, are used extensively in this process to prevent foam formation of crude oil in the gas/oil separators, thereby preventing liquid carryover with the gas and increasing capacity. The presence of foam will interfere with the accurate metering of the crude oil. In some oil fields, silicone defoamers are classed as 'critical chemicals'. Oil production could not proceed without the silicone because oil would carryover with the gas, resulting in flaring of the gas and operational shut down.

Not every crude oil foams. Foam appears to be a greater problem in high producing wells where high pressures and temperatures and high gas/oil ratios (GORs) are encountered. Foaming is a particular problem with crude oils in the North Sea.

The antifoaming performance of the silicone fluid in the gas/oil depends on two factors, viz. its solubility and its dispersibility in the oil. Generally, higher viscosity, and therefore higher molecular weight, silicones are used, usually of viscosity 12 500 cs and 60 000 cs. Should the silicone be soluble in the gas/oil mixture, it becomes a profoamer rather than a defoamer. This has to be avoided at all costs!

Generally, these higher viscosity silicone fluids are totally insoluble and indispersible in the gas/oil but, if predissolved in, say, diesel fuel before addition to the first stage separator, they will become dispersible in the gas/oil, thereby giving good antifoaming performance. Conversely, if they are either soluble or not dispersed sufficiently, at worst they could contribute more foam and at best not have any effect on the foaming propensity. Choosing the correct grade of silicone fluid and ensuring it is well dispersed is therefore absolutely vital. The concentration of silicone generally required to control foaming is between 1 and 10 ppm and even 1 ppb has been used successfully.

The latest moves to reduce the size of the new gas/oil separators or increase the capacity of existing separators, especially offshore, is making the foaming problem even more acute. This means that chemical control of foaming in gas/oil separation will become increasingly important.

5.5.7.2 Gas treatment Foaming problems are often encountered in gas processing plants. Glycols, such as ethylene glycol, are used for removing water from the gas, and aqueous solutions of amines (DEA, MEA, DGA and DIPA) or even potassium carbonate are used to extract H_2S and/or CO_2 from the gas. Corrosion inhibitors and hydrocarbon entrainment are generally the most usual sources of foam. Excessive foaming leads to high solution losses, out of specification end product, production losses and contamination of downstream processes.

To control this foam, some attention has to be put into finding the source of the foam. However, this does not always solve the problem. The use of a defoamer is then applied, and silicone emulsions, high molecular weight alcohols and even glycols are used at this stage.

5.5.7.3 Other petroleum applications Another major foaming problem is in delayed coking. Refinery bottoms are converted to useful products, coke and volatile recycled products by a thermal cracking process. Basically, the feed thickens and foams as it enters the huge coke drum at 500°C. Silicone fluids are used to control the foam, allowing faster feed rates and greater capacity in the coke drum.

Silicone antifoams, while controlling foaming well enough, have produced a side problem due to deposition of silica on the catalyst surfaces in hydrotreators. One possible explanation of this is that at the high temperatures involved in this process, nonvolatile silicones begin to revert to mixtures of volatile dimethylsiloxane cyclics which, in turn, degrade thermally to silica (SiO_2) on the catalyst surface. Because of this, attempts to reduce silicone levels in delayed coking by developing more effective silicone or silicone/organic defoamer combinations are in progress.

Other petroleum processing applications for defoamers include drilling muds where excessive foaming interferes with lubrication and lubricating oils and where, again, air entrainment and surface foam interferes with the lubrication properties of the lubricant. Also, major foaming problems requiring the use of defoamers include asphalt processing and transportation, some distillation processes and benzene/toluene/xylene extraction by glycols.

Finally, a most interesting application, which recently reached commercialisation, is defoaming of diesel fuels. In the efforts to persuade the motorist to prefer a particular type of diesel fuel, all sorts of additives have been added to the fuel to aid its performance. One of the more visible additives is a defoamer. This both prevents foaming at the bulk storage stage and, more importantly, allows the motorist to fill his tank cleanly and without the pump cutting out prematurely because of excessive foaming.

Conventional silicone antifoams were totally unacceptable as they tended to promote foam rather than suppress it. The more exotic fluorinated silicones, which are generally used in petroleum processing where solubility with silicone is a problem, while solving the problem, are very costly. Also, the presence of fluorine containing exhausts are perhaps less environmentally acceptable, although the levels of fluorine produced are very low. It has been found that certain silicone glycol block copolymers work exceptionally well in these systems at minimal cost and without any environmental risk. Further work on this interesting new application is continuing.

5.5.8 Others

A number of important industries in which foam is a serious problem have been described. This list is not exhaustive. To describe every industrial application where foam is a problem would require a whole book. However, some important industries have been left out and the following is a brief synopsis of those industries that have not been discussed in detail but do have a significant foaming problem. These are as follows:

5.5.8.1 Chemical industry

(*a*) *Distillation processes*: These often foam and can be a serious problem if the plant is being operated close to its capacity. Industries using defoamers in distillation processes include ethylene oxide manufacture, not only during CO_2 removal but also in the final separation of ethylene oxide from water.

(*b*) *Rubber latex manufacture*: Recovery of monomers from aqueous polymerisation systems can be quite a problem because of excessive foaming. The use of defoamers shortens recovery periods and eliminates recovery line blockages, with increased production efficiency. Defoamers are also used extensively in latex compounding and coating operations.

(*c*) *Phosphoric acid production*: In the production of phosphoric acid, high gas evolution rates cause excessive foaming, leading to hazardous spillages and loss of production capacity. Nonsilicone defoamers are generally used to control excessive foaming.

(*d*) *PVC manufacture*: Recovery of vinyl chloride from PVC polymerisers can produce severe foaming problems. The increasing tendency to reduce the level of vinyl chloride monomer present in the PVC has increased the tendency to foam in the process. Both silicone and nonsilicone defoamers are used successfully to control foaming in this industry.

5.5.8.2 Pharmaceutical industry The use of defoamers in the manufacture of, e.g. antibiotics, has been covered in Section 5.5.2. However, silicone based defoamers are used extensively in the preparation of antiflatulents used for the treatment of intestinal gas and bloating in humans. The action of the defoamer is thought to be able to change the surface tension of the mucus covered bubbles, allowing small bubbles to coalesce. The free gas that is formed is eliminated more easily by belching or passing flatus than do the small tenacious bubbles. Combinations of silicone defoamer with antacids produced in tablet and suspension form are readily available. The silicone defoamer alone can even be supplied in gel capsule.

The silicones and other nonsilicone type defoamers such as polyethylene oxide–propylene oxide copolymers are used extensively to cure the condition often known as frothy bloat in animals. Sometimes the products are used therapeutically as a drench (i.e. introduced into the mouth) or injected directly into the stomach. As prophylactics, the defoamers are fed to the animals on a preventative basis, either in their feedwater or on pasture on to which the defoamer is sprayed.

The very low toxicity of silicones makes them particularly acceptable to treating the human species for flatulence, and there are a number of extremely effective and toxicologically safe nonsilicone defoamers available for the animal kingdom also.

5.5.8.3 Building industry (latex and concrete) The presence of entrained air/foam in both concrete structures and concrete latex based structures is undesirable. The presence of entrained air reduces the strength of the structure and can completely spoil the surface of the concrete/latex mix particularly if the structure is a decorative one. Both silicone and nonsilicone defoamers are used in these systems and a number of powder type defoamers have been especially developed so they can be included in the concrete powder mix before being wetted.

This market area is going to be of increasing importance as only in recent times has the effect of air entrainment on the strength of concrete been fully appreciated. Also, with the increasing use of latex/concrete mixtures in, e.g. self levelling floors, entrained air/surface foam spoils the surface finish of the floors, and defoamers are increasingly being used in the formulations to reduce air entrained/foaming tendency to a minimum.

5.6 Conclusions

It is obvious from the contents of this chapter that foam is a problem common to many industries and that the overall importance of defoamers to the efficient running of industry is probably not fully appreciated. Each industry has its own particular requirements for a defoamer, not only related to its ability to control foaming efficiency in a particular system, but also to do so without any deleterious side-effects either to the product being made, mankind or our environment. As we become more environmentally aware, governments are going to demand more from the defoamers. This will undoubtedly result in a change of emphasis from some of the more traditional defoamers that are perhaps, less environmentally acceptable, to the newer types which are. The risk of change, if it is too fast, will result in extra cost burdens on industry. This will undoubtedly give a new impetus to defoamer development and we may well see a new generation of high technology defoamers being produced in the next decade.

5.7 References

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6 Corrosion inhibitor properties of surfactants

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6.1 Introduction

Most metals corrode when exposed to the atmosphere. The most common example of corrosion is that of iron in the presence of air and other chemicals; this phenomenon is known as rusting. The protection of iron against rusting can be accomplished in a number of different ways, but the most common are:

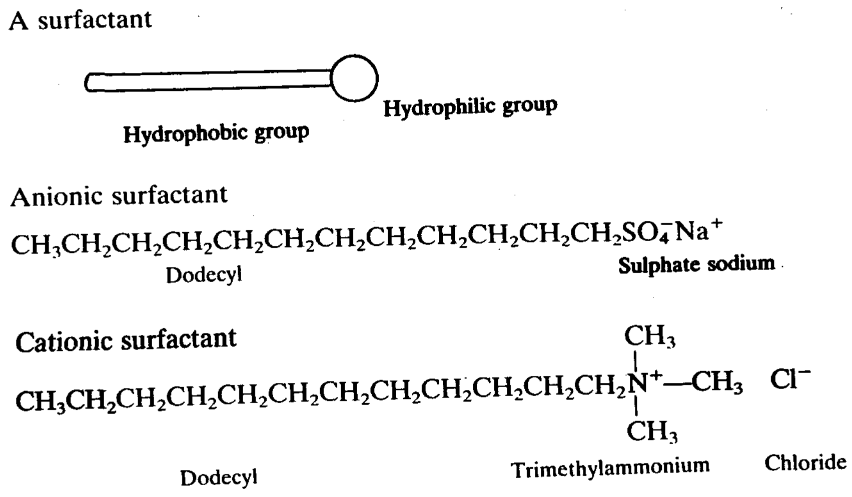
By the application of a hard durable surface coating such as paint.
By the application of a soft nondurable coating such as oil or grease.
By adding chemicals to the environment in order to protect the metal.

Hard durable coatings which contain surfactants are beyond the scope of this review and will not be discussed. One large area of application of corrosion inhibitors is in industrial and process water where inorganic or low molecular weight organic inhibitors are used, but these are not normally surfactants.

The distinctive property of a surfactant is that it is attracted to and adsorbed on the surface of iron. When so adsorbed its effective concentration at the metal/corrodent interface is much higher than that in the bulk of the liquid. The surfactant can be effective at relatively low concentrations compared to paints, oils or bulk coatings. It is this ability of the surfactant to be used at low concentrations (e.g. <0·01%) in a crude oil containing water and salt and yet provide corrosion protection to a mild steel pipeline which makes corrosion inhibition economic. However, there are other applications such as in temporary rust preventatives where the surfactant type corrosion inhibitor must be used in high concentrations. In these applications its most useful attribute is the property of the surfactant to form micellar solutions and its ability to dewet surfaces.

Typical applications where surfactant type corrosion inhibitors are used include steam and condensate systems, oil and grease additives, cutting oils, temporary rust preventatives, crude oil production, and acid pickling of iron and steel with acid.

Organic corrosion inhibitors of the surfactant type can be anionic where the anion is typically carboxyl, sulphonate or phosphate, and cationic where the cation is invariably nitrogen in the form of an amine, amide compound or quaternary (frequently as a heterocyclic). The hydrophobic part of the surfactant will be dependent on the environment in which it is operating. It is the ability of the synthetic organic chemists to manufacture products with varying oil and water solubility which makes the surfactant type products so versatile and useful. Figure 6.1 illustrates typical anionic and cationic surfactants—hydrophobic (water hating) and hydrophilic (water liking) moieties.



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2SO_4^-Na^+$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{N^+}}\text{—}CH_3 \quad Cl^-$$

Fig. 6.1 Anionic and cationic surfactants.

The mechanism by which surfactant type corrosion inhibitors work is broadly described as adsorption at the surface. In many cases, the exact nature of adsorption is not yet fully understood nor are the strong synergistic effects that are observed. Organic surfactant type corrosion inhibitors are frequently complex formulations, the ingredients of which act synergistically. A further synergism may exist between the formulation and the components of the medium in which it is deployed. Selection of inhibitor types usually involves a compromise between the maximum inhibition available from the chemical system, allowable application methods and cost.

This report gives a summary of the principal organic surfactant type corrosion inhibitors and where they are used. The present knowledge on the mechanism of action will be discussed as well as the relationship between the structure of the surfactant and its performance as a corrosion inhibitor.

6.2 Applications of surfactants as corrosion inhibitors

The examples given below do not describe the full range of applications and the organic surfactant type corrosion inhibitors used, but do illustrate the major products and the variety of chemical structures available.

6.2.1 Acid pickling of iron and steel

Steel is 'pickled' in mineral acids (e.g. strong hydrochloric acid) in order to remove mill scale. The corrosion inhibitors used at low concentrations (*c.* 0·5%) are synergistic blends of nitrogen based surfactant compounds in conjunction with lower molecular weight sulphur compounds, e.g. dibenzyl sulphide. The surfactant can be high molecular weight primary and secondary alkyl amines, quaternary ammonium compounds or ethoxylated amines. The exact choice of nitrogen derivative will depend on the temperature of use (usually 60° to 90°C), the composition of the acid (hydrochloric, sulphuric, hydrofluoric, citric, sulphamic or phosphoric) and the type of scale. The latter is important.[1] The surfactant facilitates the penetration of the pickling acid into the cracks and fissures of the scale in order to accelerate the undermining and flaking of the scales. Hydrogen is evolved if the metal is attacked by acid, and the corrosion inhibitor should minimise the production of hydrogen. The evolution of hydrogen will give a foam and it is desirable that this should be at a minimum in order to reduce the spraying of the acid and thereby avoid health hazards. A stable foam layer can be a benefit in conserving heat. The surfactant must be stable to acid conditions. In applications where the acid is applied using high pressure sprays it is desirable to eliminate the foam which could be formed by the mechanical agitation as well as by chemical reaction. Examples of these types of inhibitors are shown in Fig. 6.2.

All the products contain polar centres like nitrogen, sulphur, oxygen, heterocyclic ring systems, aromatic ring systems and triple bonds. Primary amines and secondary amines have the optimum efficiency in hydrochloric acid where the alkyl group is C_{10}–C_{12} or where the hydrophobe is an aromatic ring. The imines and aminales formed by condensation of amines with aldehydes can give good protection, but they tend to be unstable at temperatures over 60°C.

Quaternary compounds are the most important group of inhibitor compounds for acid pickling, using hydrochloric acid.[1] Typical quaternary ammonium compounds are based on ammonium, pyridinium and quinolinium ions. The highest efficiency has been found for benzyl and alkylbenzene quinolinium and isoquinolinium compounds. Most quaternaries have limited temperature stability and 70°C would be the maximum safe operating temperature.

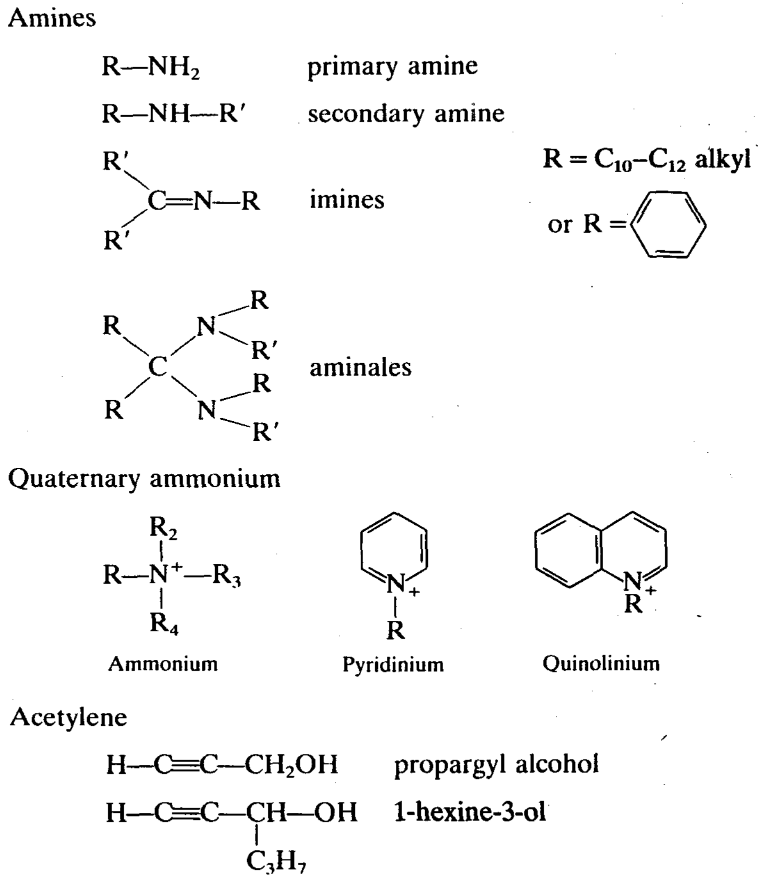


Fig. 6.2 Acidic pickling inhibitors.

Commercial nitrogen containing inhibitors frequently incorporate derivatives of acetylene such as propargyl alcohol or 1-hexine-3-ol (see Fig. 6.2). The acetylene compounds retain their efficiency at temperatures up to 100°C.

The sulphur containing inhibitor compounds include such products as sulphoxides, sulphides, mercaptans, thiocyanates and thioureas. In general, the benzyl derivatives tend to be the best corrosion inhibitors, but many products are unstable at high temperatures, giving off hydrogen sulphide which is poisonous to man and promotes hydrogen embrittlement of metals. Sulphur based products tend to be used with sulphuric acids while nitrogen derivatives are used with hydrochloric acid.

The acetylene derivatives improved inhibition performance when added to some mercaptans, e.g. 2-mercaptobenzimidazole. Acetylenic alcohols give inhibition on their own, but the efficiency is improved by addition of halide ions.

The length of the hydrocarbon chain (R in Fig. 6.2) controls the solubility of the surfactant in the solution and also the foaming behaviour.

6.2.2 Corrosion inhibitors in oil recovery

Oil production and oil transportation involve all types of corrosion, viz. in water, in oil, general corrosion, localised corrosion, pitting and corrosion in crevices and in sludge, erosion corrosion, cavitation corrosion (particularly in pumps) and fatigue. In addition, all types of bacteria can cause corrosion when accumulating on metal surfaces. Of main interest is the slime forming bacteria, sulphate reducers and iron-oxidising bacteria. Slime formers are mainly present in fresh water and grow in aerobic as well as anaerobic conditions. They cause localised corrosion. Sulphate reducing bacteria normally develop and grow in an oxygen free environment. They can, however, also develop in systems saturated with oxygen, provided they can find local anaerobic conditions. Places like crevices, scale, sludge and colonies of other bacteria can give such conditions. Sulphate reducing bacteria can be found almost anywhere. They have been found in carbonaceous rock 2000 m down in the earth. They live in the sea bottom and can be found in surface water. This means that practically all liquids handled in petroleum production can contain sulphate reducers. They reduce sulphate, sulphite or organic sulphur compounds to hydrogen sulphide, ferrous sulphide and in some cases, where organic material is consumed, acetic acid. The attack caused by sulphate reducers is of the pitting type.

Iron oxidising bacteria oxidise ferrous iron to ferric iron and are frequently found in fresh water and some brines. They need oxygen to grow and often cause slime formation. They cause corrosion by setting up corrosion cells and by creating anaerobic conditions suitable for sulphate reducers.

Formulations vary widely but concentration of inhibitor is generally in the range 5–500 ppm. In new equipment or a new oil well it is the practice to start with a high corrosion inhibitor concentration and then, after initial running, drop to a value as low as 5 ppm on a continuous addition basis.

Corrosion inhibitors can be blended with other functional products to produce 'combination' products, the most common combination being packer fluids with corrosion inhibitors and biocides for long-term protection. Therefore, compatibility with other chemicals must also be considered.[2]

6.2.2.1 Drilling Most drilling systems are aqueous, and inorganic inhibitors tend to be used as they are cheaper and efficient. Oil based muds are also used in drilling, in which case an organic oil soluble inhibitor would have to be used; such products are similar to the products utilised in crude oil recovery.

6.2.2.2 Acidising Acid solutions are used to attack the rock formation in order to improve the flow of oil through the fissures in the rock. The acids used are similar to those used in acid pickling, as are the corrosion inhibitors.

6.2.2.3 Crude oil recovery and transportation

(*a*) *Primary production*: At some point in time an oil well will need corrosion inhibitors. As a well ages, the ratio of water to oil increases and the corrosivity increases. The primary cause of corrosion is due to the aqueous phase which can contain carbon dioxide, hydrogen sulphide or low molecular weight organic acids. The presence of dissolved gas in both the oil and water phases will have a marked effect on corrosivity. So long as the metal surface is covered with the crude oil, corrosion is minimal. Corrosion problems occur when the metal surface becomes wetted by the aqueous phase. The water produced with the oil is generally a brine solution containing from 1 to 40% concentration of mixed chlorides of sodium, calcium, barium and magnesium. In addition, considerable quantities of sulphate ions are present. Carbon dioxide is invariably present, but if hydrogen sulphide is also present then the well is considered 'sour', if not it is 'sweet'.

Sour wells are more corrosive. The pH of the system has a significant effect, a pH of less than 6 being more corrosive.

Gas wells are a major problem, as these have a high gas/oil ratio under high pressure. The active agent is usually carbon dioxide although the presence of organic acids causes carbon dioxide attack to occur at lower concentrations than in their absence.

The high corrosion in oil wells is not only due to corrosive gases contained in crude oil together with salt water, but also the high temperatures (up to 150°C for deep wells) and the high pressures encountered. Steel materials will corrode and crack to give sulphide stress corrosion cracks and hydrogen induced cracks. The former are apt to occur in deep wells at depths of 9000 ft (2743 m) or more. There are many variations in the conditions at the bottom of the well, e.g. wide variations in the composition of the crude oil plus large variations in the water/oil ratio. Thus, a wide variety of surfactants must be available to meet the different conditions. The first stage after recovery of the crude oil will be the separation of the salt water. The crude oil is still saturated with salt water and an oil soluble corrosion inhibitor must be used.

The length of the hydrocarbon chain (R in Fig. 6.3) controls the solubility of the surfactant in the oil/water mixtures. The longer the chain the less soluble in water and the more soluble in oil. Generally, R will be a longer chain (C_{16}–C_{18}) than those for acid pickling (see Fig. 6.2) in order to obtain some solubility in the oil phase. Changing the length of the alkyl chain can dramatically affect the partition of a surfactant between oil and water, and an increase in two methylene units can cause a 10-fold change in the partition coefficients.[2] However, changing the hydrophobic part of the molecule is less easy in practice than changing the hydrophilic group and there will be a limited range of alkyl or hydrophobic groups available at a reasonable cost.

In order to provide a range of corrosion inhibitors for the varying conditions there is a need to vary and control the extent of water solubility. Several systems have been developed where the surfactant molecule may be gradually changed from an oil soluble into a water soluble molecule by chemical modification. These systems are illustrated in Fig. 6.3.

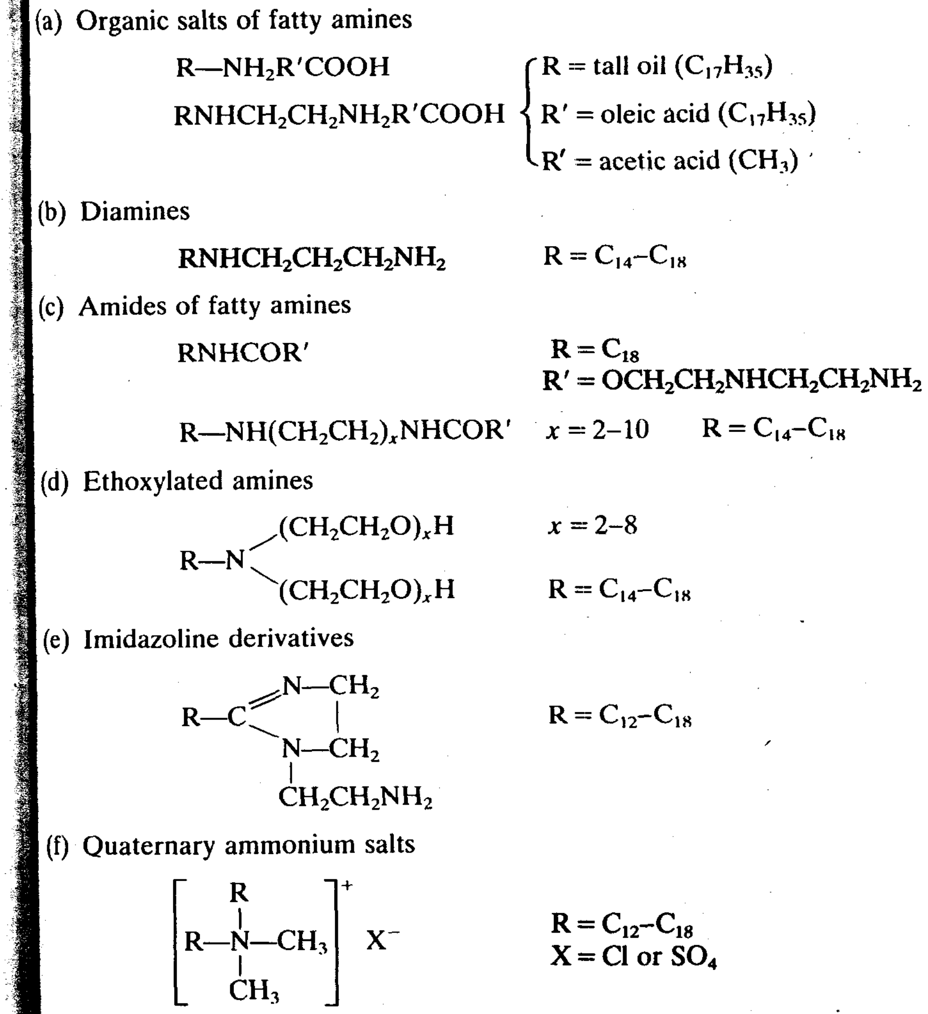


Fig. 6.3 Corrosion inhibitors for crude oil.

1. The major products used are long chain fatty amines which are normally oil soluble. The amines can be primary amines or diamines. Their solubilities can then be changed by the formation of salts with various acids; acetic acid will normally give water soluble salts while tall oil fatty acid salts will be oil soluble. (See Fig. 6.3(a).)
2. Reaction of a primary amine with acrylonitrile, and the product hydrogenated, gives an alkyl propylenediamine which has in-

creased water solubility due to the two polar sites. (See Fig. 6.3(b).)

3. The formation of amides with long chain fatty acids will give oil soluble products, but if an amide is prepared with hydroxyethylethylenediamine then a water dispersible product is formed. (See Fig. 6.3(c).)
4. Ethoxylation of the amine can also confer water solubility on the amine, the more ethylene oxide the greater the water solubility. (See Fig. 6.3(d).) The products are soluble over a wide pH range and cationic at low pH.
5. Imidazoline formation (see Fig. 6.3(e)) from fatty acids will give water dispersibility. Subsequent reaction with ethylene oxide can then give increased water solubility.
6. Quaternary ammonium compounds (see Fig. 6.3(f)) are normally water dispersible due to the strongly charged nitrogen ion. Such products can also exhibit bacteriostatic properties.

(*b*) *Secondary recovery* (*waterflooding*): Secondary recovery consists of forcing water into the ground in a number of wells in a fixed pattern in order to force oil up through a central well. The water usually used is either seawater, in the case of offshore wells or water which has been produced from the well. The water is corrosive and contains oxygen, salt and bacteria, all of which are corrosive. The bacteria most responsible for corrosion are the sulphate reducing bacteria. Amine based surfactant and quaternaries are used as combined dispersing agents and bactericides. Typical quaternaries are trimethyldodecyl ammonium chloride and dimethyldodecylbenzyl ammonium chloride.

Bessems and Clemmit[3] showed that quaternaries are more effective than the amine or ethoxylated amines. The corrosion inhibition system must be water soluble and also be compatible with other components such as oxygen scavengers, bacteriostats and dispersing agents. The technique of producing water solubility in the corrosion inhibitor is similar to that described above.

(*c*) *Storage and transport*: Crude oil storage-tank pipelines are subject to all the problems of primary production while the refined product often contains some water.

6.2.2.4 Refineries Refineries have to deal with gases, aqueous solutions, oil/water mixtures and oil. They will be using a wide variety of corrosion inhibitors, but these will be generally similar to those chemicals already described.

6.2.3 Temporary rust preventatives

These are products applied to metal parts to provide protection from rusting and sometimes may need refinishing, e.g. painting. Examples of such products are:

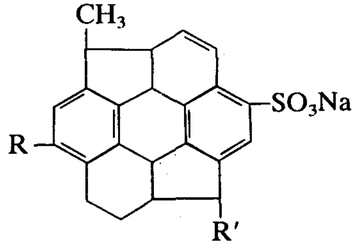
Oil based	—slushing or milling oils, protection of sheet steel, running in lubricants for cars
Solvent based	—protection of metal tools and engineering components
Greases	—gears, chains, cables, where good lubrication is needed
Waxes	—exposed underbody of cars
Water soluble	—slowly replacing solvent based.

The type of surfactants in these products must be oil soluble and, therefore, the molecular weight of the hydrophobic portion is higher. In general, anionic type products are used rather than cationic and a description of the more common type is given in Fig. 6.4.

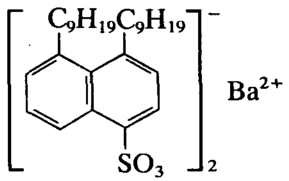
Combinations of these additives, particularly sulphonates with oxidates or acids, produce synergistic effects in special applications. All petroleum oils do not have the same response to a particular corrosion inhibitor combination and varying efficiencies can be found in various base oils. It is difficult to characterise the mineral oil used exactly because of the nonspecific descriptions as naphthenic or paraffinic by the suppliers. Therefore, it is difficult to relate performance in a given oil to the composition of the oil. The art of formulating rust preventatives is entirely empirical. What is known is that the higher the viscosity of the oil, the heavier the film and the greater the degree of protection. Therefore, within limits prescribed by handling and application methods, the highest viscosity oil acceptable should be used.

In many applications the rust preventative is applied to metal surfaces which are wet with water and therefore the treatment must remove the water and wet the metal surface with the oil, grease or wax to act as a barrier for any water attack. The surfactant must, therefore, act as a dewatering agent as well as a corrosion inhibitor.

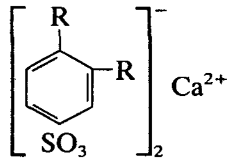
Sulphonates



Petroleum sulphonates



Barium dinonyl naphthalenesulphonate



Calcium dialkyl benzene-sulphonate ($R = C_{10}–C_{14}$)

Oxidised waxes

'Oxidates'— oxidised petroleum fractions

Fatty acids and esters

Tallow fatty acid $C_{17}H_{35}COOH$

Fig. 6.4 Active ingredients in temporary rust preservatives.

6.2.4 Lubricating oils and greases

The internal combustion automobile engine produces water, unburned gasoline, organic acids, inorganic acids, sludge and varnishes all of which will accumulate in the engine/lubrication system unless kept separate. However, these combustion residues do slowly get into the lubrication system. Lubricant additives are needed to retard the formation of the harmful by-products and also to neutralise the adverse effects and help prevent damage to the engine system. Antioxidants, corrosion inhibitors, detergents, dispersants, antifoams, viscosity index improvers and antiwear additives are all present in a modern engine oil additive. Some additives perform more than one function, e.g. oil soluble sulphonates which can act as detergent, dispersant and corrosion inhibitor.

The formation of inorganic acids leads directly to corrosive wear. Particularly critical is the formation of sulphuric acid from high sulphur content diesel fuel. Acids can lead to rusting in critical moving parts such as valve lifters. The oil additives contain inorganic bases in a colloidal form which can neutralise the free acids. The bases are commonly calcium, barium or magnesium oxide or carbonate at 20 to 35% by weight in the additive concentrate, with mineral oil as the medium. They are stabilised by 18 to 30% by weight of oil soluble surfactant. This concentrate will be used at 1·5% by weight of lubricating oil in internal combustion engines for cars, but up to 30% by weight in marine diesel engine lubricants.

The surfactants disperse and stabilise the base in the lubricating oil. The most common surfactants are alkylbenzene sulphonates and sulphurised alkyl phenols. The alkyl group of the alkylbenzene is typically C_{24} (made by oligomerisation of propylene or butene) or a linear olefin with a chain length greater than C_{18}.

Sulphurised alkyl phenols are derived from tetrapropylene-phenol. The alkyl phenol can be sulphurised by reaction with sulphuryl chloride or, alternatively, the sodium or calcium phenates will react with elemental sulphur. The products are complex mixtures with an average of more than one sulphur atom in the sulphur bridges linking the phenol groups. Other surfactants in commercial use are the long chain alkyl salicylates or naphthenates. The sulphonates and naphthenates will also act as corrosion inhibitors.

Greases and oils used for bearings and gears contain corrosion inhibitors, principally to protect the metal surfaces from organic acids formed by oxidation or when moisture enters the system. All modern oils and greases will have high additive packages and these can sometimes emulsify the water into the oil thereby giving a greater surface area of water to wet the metal. This must be avoided, so oil soluble surfactants which show good demulsification properties are preferred, e.g. barium dinonylnaphthalene sulphonate. There is a distinction between corrosion from the organic acids and rusting due to water. Zinc dialkyldithiophosphate gives both antioxidant and protective action against oxidation while neutral high molecular weight barium and calcium sulphonates are used to protect against rust.

Hydraulic oils will need similar corrosion inhibition to bearing oils and will require similar types of corrosion inhibitors. Long chain oleate esters can also be used in critical cases (hydraulic valve lifters).

The role of the corrosion inhibitor must be to keep the metal surfaces wet with oil and to keep the water in a nonemulsified form. There is considerable secrecy surrounding the type of corrosion inhibitor in lubricating oils and greases, but most of the products shown in Fig. 6.4 will be used.

6.2.5 *Cutting oils and metal working*

Metal working involves the cutting or deformation of metal. In order to reduce the heat, aqueous solutions or emulsions are used as lubricants and coolants. The most common products are 'soluble oils' which are in fact dilute emulsions of mineral oils in water. The emulsifying agents used also act as corrosion inhibitors, and Fig. 6.5 gives a list of the emulsifiers/corrosion inhibitors used. The degree of protection needed is small and if more protection is needed then the metal parts would be treated with one of the temporary rust preventatives.

Corrosion inhibitors with emulsifying properties

Petroleum sulphonates	Mol. wt 420–475—sodium salt
Fatty acid soaps	$C_{17}H_{35}COO^-$— sodium or alkanolamine soap
Alkanolamides	$RCONH(CH_2CH_2OH)_2$ $R = C_{17}H_5$ from tall oil or tallow

Corrosion inhibitors

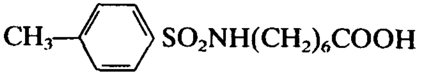
Dimer acids	$HOOC(CH_2)_xCOOH \quad x = 10–12$
Aryl sulphonamide carboxylic acid	
Phosphate esters	$ROPO_4$ amine salt with $R = C_{14}–C_{18}$ or $C_{12}–C_{14}$ alcohol + ethylene oxide

Fig. 6.5 Corrosion inhibitors/emulsifiers used in metal working.

6.3 Mechanism of corrosion

Corrosion occurs when a metal changes to a more stable state, the most common example being that of the metal iron, which will oxidise in an atmosphere containing oxygen to form the oxide known as rust.

Metal→ more chemical stable state

Iron→ Iron oxide(rust)

The corrosion of iron to form rust will only occur in the presence of electrolytes and water. An equilibrium is set up:

$$M \rightarrow M^{n+} + ne^-$$

$$\leftarrow$$

→ Corrosion

← Noncorrosion

Thus, the reaction goes to the right (corrosion occurs) if electrons are removed from the metal.

In rusting, iron loses electrons and goes to the positively charged state:

$$Fe \rightarrow Fe_2 + 2e^-$$

oxygen and water react to form the hydroxyl ion:

$$O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

the overall reaction is

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 + O_2 \rightarrow RUST$$

Three steps are necessary for rusting to occur.

(1) Loss of electrons or anode oxidation.
(2) Consumption of electrons or cathode reduction.
(3) Ion transfer through the electrolyte.

If any of these processes can be stopped then corrosion will stop.

A surfactant is added to the corrosive environment, e.g. crude oil, or is present in a corrosion inhibitor, e.g. a temporary rust preventative. In either case the surfactant is adsorbed (or chemisorbed) on to the metal surface from the liquid and then subsequently disrupts in some way the corrosion mechanism.

There has been considerable discussion on the exact mechanism by which corrosion inhibitors work, but there would seem to be no doubt that surfactants must first get near the anode and/or cathode reaction sites and then change the electrical double layer which is present at the metal/solution interface and/or create a physical barrier to the diffusion of ions and reactants to and from the metal surface.

6.3.1 Adsorption of surfactants

In a large number of applications the surfactant type corrosion inhibitors are used in very low concentrations of the order of 5 to 50 ppm. In order for them to function at this concentration there must be adsorption from solution on to the metal to give a high concentration at the metal surface. If a chemical bond is formed between the surfactant and the metal surface then chemisorption takes place.

Adsorption on to surfaces is the primary property of surfactants. The observed phenomenon is that a surfactant will have a higher concentration at a phase boundary than that in the bulk of the liquid. Thus, as shown in Fig. 6.6, there will be a concentration of surfactant on a metal surface immersed in a solution of a surfactant.

The surfactant in solution is present as free molecules and, above a certain concentration, as micelles. Micelles are only formed above a certain concentration known as the critical micelle concentration (CMC). Micelles are usually spherical but can change shape to rod-like assemblages and packed layers at higher concentrations. (See Fig. 6.7.) Some typical critical micelles concentrations are:

Aqueous solution	
Dodecyl trimethylammonium bromide	0·42%
Sodium dodecyl sulphate	0·24%
Nonaqueous	
Dodecylammonium octanoate (in benzene)	0·75%
Sodium dinonylnaphthalene sulphonate (in benzene)	0·005%

Micelles are formed in solvent solutions as well as in water. There are very little data available for micelles in hydrocarbons, but that which is available would indicate that micelles are formed at low concentrations but with a smaller size than in aqueous solution.

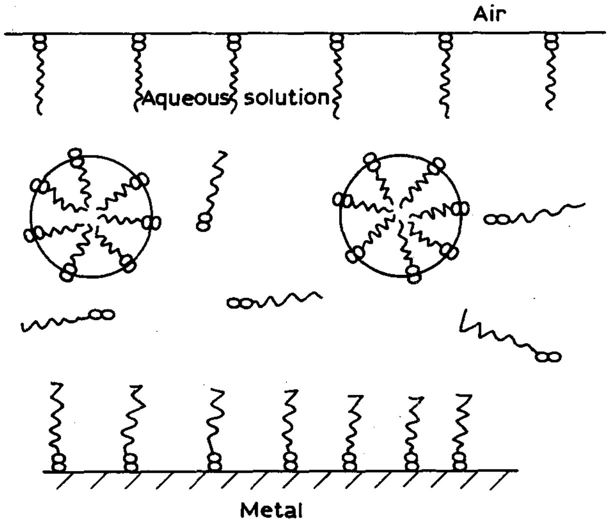


Fig. 6.6 Adsorption of surfactant on to a surface.

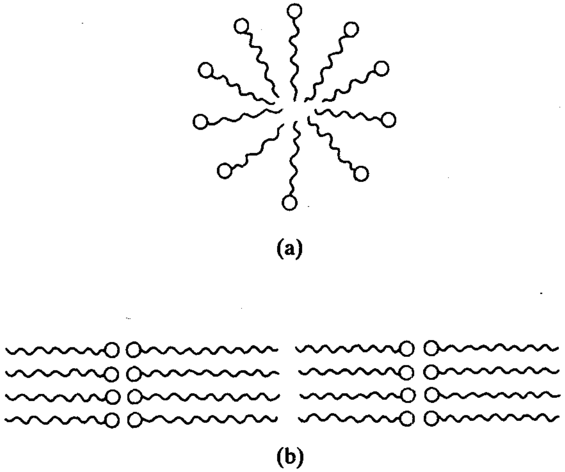


Fig. 6.7 Micelle formation: (a) spherical (in water); (b) lamellar.

The process of adsorption is not simple. It depends on:

(1) The chemical nature of the adsorbing species.
(2) The nature of the solid surface.
(3) The nature of the liquid environment.

There are five principal mechanisms which can control adsorption.

(1) Ion exchange with the electrical double layer.
(2) Ion pair formation with the electrical double layer.
(3) Polarisation of π electrons.
(4) Hydrogen bonding.
(5) van der Waals dispersion forces.

Figure 6.8 illustrates these mechanisms in diagrammatic form.

For a more detailed description of adsorption of surfactants on surfaces see Myers.[4] There is no intention to describe adsorption mechanisms in detail but rather to point out the complexity of the adsorption process. In mechanisms 1, 2 and 3 in Fig. 6.8, polar forces are involved, so the nature of the ionic group would be expected to be the main characteristic if ion exchange, ion pair formation or polarisation of π electrons are the controlling mechanism for adsorption. Mechanisms 1 and 2 need a strong polar ion. In the case of polarisation of π electrons (mechanism 3) nitrogen with a lone pair of electrons is an efficient atom for attachment to metals. The size and shape of the hydrophobic groups would be expected to affect the different types of adsorption by two ways, viz. varying the solubility of the polar portion and sterically packing together. Empirically, it has been found that the most effective surfactant type corrosion inhibitors are anionic or cationic and that nonionic surfactants are not as effective. It is recognised that this is a broad generalisation and there could well be exceptions.

These proposed mechanisms explain how the surfactant concentrates at the metal/liquid interface but give no indication on how it disrupts the process of corrosion. If the disruption of the process is by way of a physical barrier to stop the transport of ions to and from the surface then the packing and the structure of the surfactant should become an important factor. It is worth pointing out that recent views on the mechanism of the formation of microemulsions are related to the relative cross-sectional areas of the hydrophobic and hydrophilic groups.[5] Similar mechanisms might play a part in the formation of barriers to the corrosion process. It is unlikely that one simple mechanism will explain the different applications and different types of surfactant which are used. However, the shape and size of the hydrophobic group of the surfactant and the number and strength of ionic groups will all be important factors in the efficiency of the surfactant as a corrosion inhibitor.

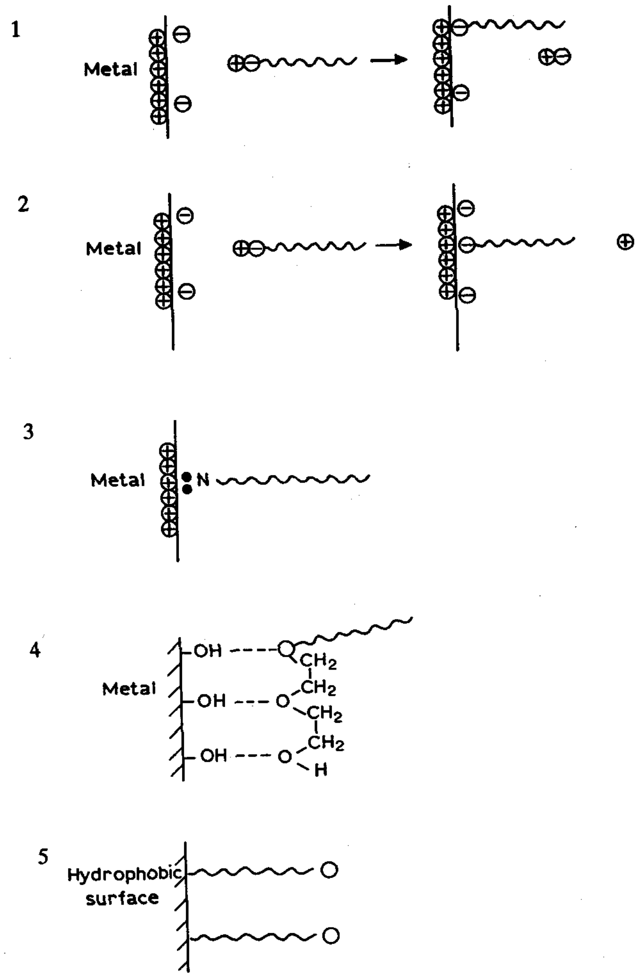


Fig. 6.8 Mechanism of adsorption. 1, Ion exchange; 2, ion pair; 3, polarisation of π electrons; 4, hydrogen bonding; 5, van der Waals forces.

6.3.2 *Adsorption and chemisorption*

Many authors have, in the past, attempted to distinguish between adsorption and chemisorption, the latter being where chemical reaction takes place between the metal and the corrosion inhibitor, e.g. formation of a metal salt. However, this distinction does not help in explaining the majority of the observed phenomena, particularly in the efficiency and synergism of mixtures of surfactants. More recently, the concept of ordered adsorption on surfaces such as hemimicelles (see Fig. 6.9 and Rosen[6]) has been put forward, which would be expected to be bound more firmly than single molecules and possibly be more effective in acting as a barrier for ions.

Lorenz and Mansfield[7] have attempted to classify different types of inhibition mechanism as interface and interphase inhibition. Interface inhibition is by specific adsorption, forming two-dimensional layers on the corroding surface, while interphase inhibition is caused by a three-dimensional protective layer in which the inhibitor is incorporated. The interface type can be subdivided into:

Geometric blocking
Deactivating
Reactive (chemisorption?)

The inhibition efficiency (I):

$$I(E, c_i, t) = \frac{d(E, t) - d_i(E, c_i, t)}{d(E, t)} \qquad (6.1)$$

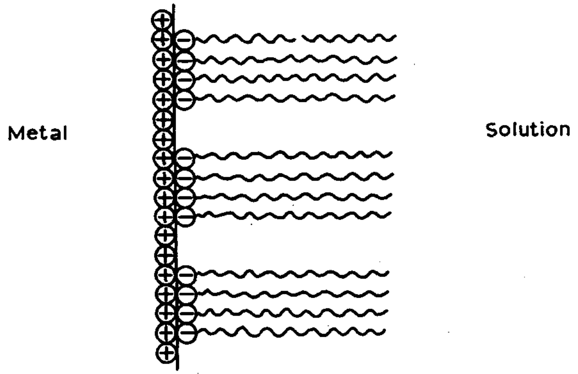


Fig. 6.9 Hemimicelle structure.

where E = electrode potential, c_i = inhibitor concentration, t = exposure time, d = current density in absence of inhibitor, and d_i = current density in presence of inhibitor.

Interface inhibition presumes a strong interaction between the corroding substrate and the inhibitor. The authors describe[7] how these two cases may be distinguished theoretically.

6.3.2.1 *Geometric blocking*

This represents an adsorbed monolayer of defined structure and, if the proportion of the electrode covered is θ, then

$$d_i = d(1 - \theta) \qquad (6.2)$$

where

$$\theta = \frac{\text{Potential dependent concentration of inhibitor}}{\text{Saturation value}} \qquad (6.3)$$

Thus, from eqn (6.1):

$$I = \theta = 1 \text{ (i.e. complete inhibition for complete coverage)}$$

6.3.2.2 *Blocking of active sites*

This represents low average coverage, but if the adsorbing species is adsorbed preferentially at the active sites then the inhibitor efficiency may still be high. The adsorbate is not inert but reactive. Two different cases of reactive coverage may be distinguished:

1. The inhibitor acts as a positive or negative electrocatalyst for the corrosion reaction.
2. The adsorbate itself undergoes a redox process, and primary or secondary inhibition can occur depending on the retardation effects caused by the original adsorbate and/or its reaction products.

In this case

$$\text{Inhibition} \quad \theta \leqslant I(\theta) \leqslant 1 \qquad (6.4)$$

$$\text{Stimulation} \quad I(\theta) \leqslant 0 \qquad (6.5)$$

Interface inhibition is mostly observed in corrosion systems with the bare metal surface in contact with the corrosive medium (e.g. acid pickling).

The use of this theory is basically to explain the observed electrochemical measurements on these systems. The authors conclude[7] that a distinction between geometric blocking and blocking of active sites is not possible by simple steady-state DC measurements. These authors[7] have pointed out the possible complexity of the adsorption process and that in fact the chemisorption could well be identified either with $\theta = 1$ (i.e. efficient coverage) or with blocking of active sites. Nevertheless, it is not necessary to invoke chemisorption in order to achieve complete coverage of surfaces by surfactants.

Adsorption, a purely physical mechanism, can change to chemisorption where the surfactant undergoes a chemical reaction with the substrate. The actual reaction of a surfactant with a substrate is not easy to differentiate from strong adsorption, but recent workers[8,9] have indicated the existence of the formation of surface chelation of *n*-oleoyl sarcosine on a steel surface. The hydrocarbon chain is tilted at an angle and forms a monomolecular film. However, Ref. 9 shows that an additional molecular layer is found in the presence of divalent cations. There would seem to be no evidence to suggest that chemisorption (as distinct from adsorption) is necessary for efficient corrosion inhibition. However, chemisorption may well be important in the retention of corrosion inhibition in conditions where the environment might well favour desorption.

To conclude, the theoretical explanation of how surfactants function as corrosion inhibitors does not help in giving a full explanation of observed phenomena or in enabling predictions to be made in the formulation of better corrosion inhibitors. Nevertheless, a large amount of empirical data has been generated which helps to correlate the inhibition performance with chemical structure. Unfortunately, most of the data are kept inside commercial companies and very little is published. The next section will describe what is available.

6.4 Corrosion inhibitors used in aqueous systems

6.4.1 Corrosion inhibitors used in acid solution

An acid solution is one of the simplest systems to try and understand as there is only the aqueous solution of the acid and the metal surface. However, the metal surface can be very different from one application to another. Corrosion in acid solution has practical importance due to the applications of acid pickling of iron and steel, chemical cleaning of scale or deposits in boilers and heat exchangers, and acidising in oil recovery.

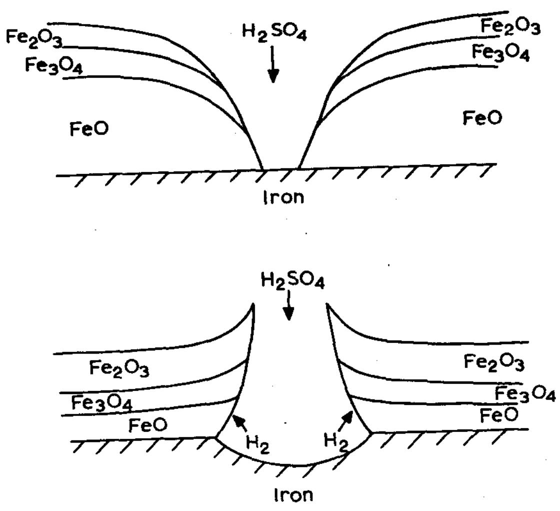


Fig. 6.10 Rust and acid cleaning.

The surface of iron that becomes covered with rust has a complex structure (Fig. 6.10). Low carbon steel has a covering of rust which is composed of an upper layer of hematite, a middle layer of magnetite, and the layer in contact with the metal being ferrous oxide. The last is more soluble in mineral acids than the other oxides so that if the acid can penetrate the top layers it can quickly dissolve the ferrous oxide and react with the bare metal. The hydrogen, which is formed by reaction of acid with the iron, can help to lift off the upper layers of scale. However, the inhibitor should reduce the amount of iron dissolution and prevent hydrogen adsorption by the iron. It has been found in practice that there is no correlation between inhibition of metal dissolution and inhibition of hydrogen penetration into the metal.

Effective inhibitors used in acid pickling to remove mill scale are complex mixtures of more than one inhibitor substance plus a surfactant which functions as a wetting or foaming aid plus anions which act synergistically plus cosolvents to aid the solubility of the organic compounds. The types of chemicals used as corrosion inhibitors have been already described in Section 6.2.1. For a detailed description of the types of compositions see Schmitt.[1]

Wetting agents, detergents and foaming agents are also needed. In practice, one surfactant alone cannot provide all the necessary properties, and mixtures of surfactants are necessary. Compatibility becomes a problem if cationics are used for corrosion inhibition and anionics are used for foaming and wetting. At the present time there are now amphoteric surfactants being used which can be compatible with both anionics and cationics. The particular products being used are nitrogen based when hydrochloric acid is used, while sulphur based chemicals are used with sulphuric acid pickling.

The most effective inhibitors are the quaternary ammonium compounds, but only when used in the presence of chloride, bromide or iodide, the last being the most effective. The most effective structure for the quaternary is where there is at least one C_{10}–C_{12} alkyl chain and one benzyl group attached to the nitrogen. It may be a coincidence, but the most widely used quaternary ammonium compound, benzalkonium chloride, has a very similar structure, this latter product being widely used for its antibactericidal properties. Particularly high efficiency is claimed for benzyl and alkyl benzyl quinoline and isoquinoline groups. The quaternaries used are soluble in water or acid.

There seems little doubt that adsorption of the surfactant type corrosion inhibitor is necessary for it to function efficiently. However, the exact mechanism of adsorption is still not clear. Schmitt and Bedbur[10] postulated that there were two different kinds of adsorption, viz. cooperative and competitive. They measured the effect of various quaternary ammonium compounds as corrosion inhibitors for iron in 10% HCl. The corrosion rate was measured by AC impedance, mass loss measurements and solution analysis by atomic adsorption. They concluded that the most effective quaternary ammonium compounds were when the nitrogen atom was part of an aromatic ring system and that the corrosion inhibition increased with increasing number of aromatic systems in the molecule. They also emphasised the dielectric effects exerted by the molecule after adsorption. However, it was noted that the measurements of the polarisation resistance were quite different, depending on whether the iron was exposed to the acid and the inhibitor then added or whether the iron was exposed to the acid with inhibitor added. These corrosion rates have been shown to correlate well with weight loss measurements and solution analysis by atomic absorption. The authors[10] attributed this difference to cooperative adsorption and competitive adsorption.

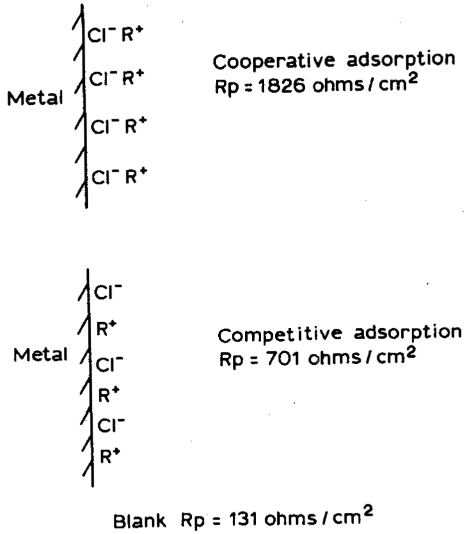


Fig. 6.11 Cooperative and competitive adsorption. (R^+Cl^- = 4-chlorobenzylquinolinium chloride.)

In Fig. 6.11, R_p is the polarisation resistance and corrosion rates are inversely proportional to R_p; thus, the cooperative adsorption gave superior results to the competitive adsorption. The diagram illustrates the speculation of the authors[10] as there was no direct proof that such types of adsorption took place. Nevertheless, in comparing Figs 6.8 and 6.11 there would seem to be similarities between these two descriptions of adsorption. On purely geometric considerations the cooperative adsorption would be expected to provide a more hydrophobic surface so long as the hydrophobic groups packed together in an efficient manner.

Szuer and Brandt[11] found outstanding inhibition using fatty acid/amine mixtures in atmospheres producing acidic condensate on the surface. The efficiency is claimed to be due to the multilayer adsorbate on the metal surface consisting of primarily adsorbed fatty acid molecules and successively cosorbed amine and further acid chains. This mechanism shows that vertical adsorption of the fatty acid appears preferential and is necessary for the formation of the multilayer adsorbate. This mechanism could explain the widespread use of the amine salts of long chain fatty acids.

Szuer and Brandt[12] summarised older work and pointed out the complexity of the adsorption process. They carried out experimental work on the adsorption of amine salts of oleic acid. The amines being aminoethylamine, morpholine, aniline, triethanolamine and triethylamine. All measurements were carried out in 0·5 M sulphuric acid. They showed that the oleic acid had the lowest free energy of adsorption when compared with the amines alone. When the salts were used all the salts tested had lower free energies than the oleic acid.

Product	*Standard free energy of adsorption (kJ/mol)*
Oleic acid (OA)	−29·4
Aniline (A)	−25·3
Triethanolamine (TEOA)	−22·5
N-(2-aminoethyl) morpholine (AEM)	−19·2
OA/A	−33·05
OA/TEOA	−33·09
OA/AEM	−33·05

The authors concluded that the adsorption proceeds through the physical bonding between oleic acid and the iron surface, turning to chemisorption, depending on the structure of the amine. Those amines with more than two functional groups give chemisorption and tight multilayer adsorbates. However, these conclusions were based on the interpretation of the electrochemical data.

6.4.2 Structure performance correlations of nitrogenous based corrosion inhibitors

The main film forming corrosion inhibitors in aqueous solution are the nitrogenous compounds. Although the exact mechanism of adsorption is not clear there is now enough evidence to show that there must be initial adsorption of the corrosion inhibitor. This then becomes firmly bound to the surface to form a bonded hydrophobic film which acts as a barrier to the migration of ions into or away from the metal coating. There have been a number of publications on the correlation between the chemical structure and inhibitor performance in aqueous systems and the main factors are summarised below.

6.4.2.1 Chain length The criteria for efficient adsorption correlates with inhibition efficiency. Thus, Nathan[13] reports inhibition efficiency in the order ethyl < butyl < hexyl < heptyl < octyl < decyl for primary amines in inhibiting the attack of acids.

6.4.2.2 Orientation Recent advances in experimental techniques in surface analysis permit more detailed examination. Salensky *et al.*[8] used a combination of infrared spectroscopy, ellipsometry and electron spectroscopy to define the molecular orientation of oleoyl sarcosine on a polished steel surface. The sarcosine group chelates to the metal to form a five-membered ring which then orients the alkyl chain to an angle of 70° to the metal surface. Fatty acids adsorbed on to aluminium oxide are oriented to 80° to the metal surface (see Allera[14]).

6.4.2.3 Chain branching Branching whether at the nitrogen atom with primary, secondary and tertiary amines or in the alkyl chain is detrimental.[15] Its effect is two-fold since branching generally leads to an increase in CMC[16] and prevents the formation of close packed hydrocarbon films. The detrimental effect of branching in the hydrocarbon chain is reported to decrease as the point of branching is moved away from the adsorbing site.[17]

6.4.2.4 Cyclisation Cyclisation can give rise to improved inhibition depending on ring size. Thus, Hackerman *et al.*[18] reported that octa- and deca-methyleneimines gave considerably better inhibition than their noncyclic analogues di-*n*-butylamine and di-*n*-amylamine, whereas the smaller ringed hexamethyleneimine was not significantly superior to di-*n*-propylamine. This phenomenon was attributed to a geometric effect in the large rings which increases the availability of the nitrogen electron pair for metal–nitrogen bond formation. However, an alternative explanation could be one of better packing of the cyclic rings to form hemimicelle-like structures (see Section 6.3).

6.5 Corrosion inhibitors used in oil/water systems

6.5.1 Oil and gas fields

Surfactant type corrosion inhibitors are extensively used to prevent corrosion in environments where there are at least two liquid phases of water in oil or oil in water. The great advantage of the film forming or surfactant type inhibitors is the ability of the formulator to choose surfactants which distribute between the oil and water phases.

The presence of micelles (see Section 6.3) can significantly affect the properties of the components in oil/water mixes. Organic oils, normally insoluble in water, will 'dissolve' in aqueous solutions of surfactants to give clear and apparently homogeneous solutions. The amount which will dissolve depends on the chemical nature of the oil and that of the surfactant. This process is known as solubilisation and is illustrated in Fig. 6.12.

As shown in the diagram the oil enters into the interior of the micelle until the concentration of oil or surfactant is such that the micelle becomes unstable and the oil then exists as a separate phase. If the amount of oil is small compared to the concentration of micelles then the oil is 'locked' into the micelle. However, such solubilised systems are dynamic as are the parent micelles, and the location of specific molecules in the micelle can change rapidly.[19]

In oil systems contaminated with water, micelles are formed but with the ionic group on the inside rather than on the outside, as in Fig. 6.12. These micelles are known as reverse micelles (see Fig. 6.13).

In exactly the same way as for solubilisation, water can be solubilised into the interior of the micelles. This property is extremely useful in dewatering wet metal surfaces with surfactants in solvent solutions (see Section 6.6).

The recovery of crude oil and the refining of oil illustrates possibly every variation in composition between oil slightly contaminated with water to water slightly contaminated with oil. A considerable amount of crude oil is extracted with typically 10 to 40% water, the water generally being heavily loaded with metal ions.

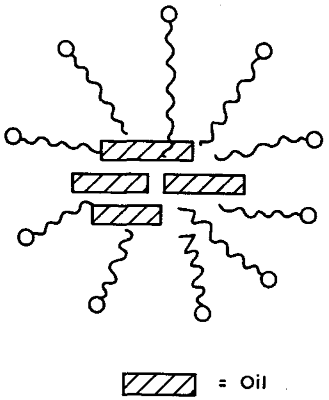


Fig. 6.12 Solubilisation.

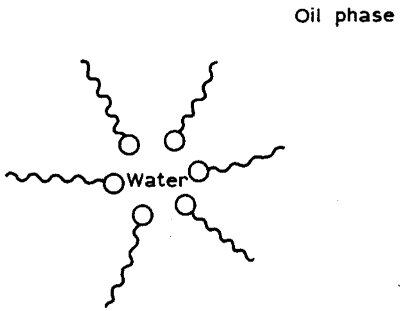


Fig. 6.13 Reverse micelles.

The performance of the corrosion inhibitor will depend on its solubility in oil and the water and can even depend on the constitution of the oil. Jasinski[20] investigated the carbon dioxide corrosion of steel in crude oil/brine mixtures and referred to references where attempts have been made to predict corrosion performance based on the inorganic chemicals in the aqueous phase of such mixtures. Jasinski pointed out that the composition of the crude oil must also be taken into account and that some of the crude oils tested acted as if they had film forming inhibitors present to inhibit corrosion.

In addition, different methods of application of the corrosion inhibitor to oil wells can require different properties of the treatment solution. In continuous addition the corrosion inhibitor must be soluble or at least miscible with the crude oil and yet adsorb on to the metal of the well. However, continuous treatment is not always possible so batch methods of treatment of the well or the formation (squeeze treatment) will be necessary. In this case the solubility in the producing fluid must be at a minimum or else the corrosion inhibitor will be quickly washed out of the well and the batch treatment must be repeated. Thus, different application methods demand different solubility properties of the corrosion inhibitor.

The situation is, therefore, much more complex than the corrosion inhibition of an acid solution as described above. It has been shown that corrosion is not severe in most cases while the metal is wetted with oil rather than the aqueous solution. Thus, the role of the surfactant in aiding or preventing the wetting of metal with water is crucial to understanding the function played by the surfactant. In addition, if the metal is wetted by the oil then the corrosion inhibitor should be oil soluble and yet be capable of being adsorbed on to the metal from the oil. Thus, the film forming corrosion inhibitor will be somewhat different in properties to those described for aqueous acid inhibition.

The types of inhibitors used are similar to the ones used in acid solution in being nitrogenous but different in detail. Thus:

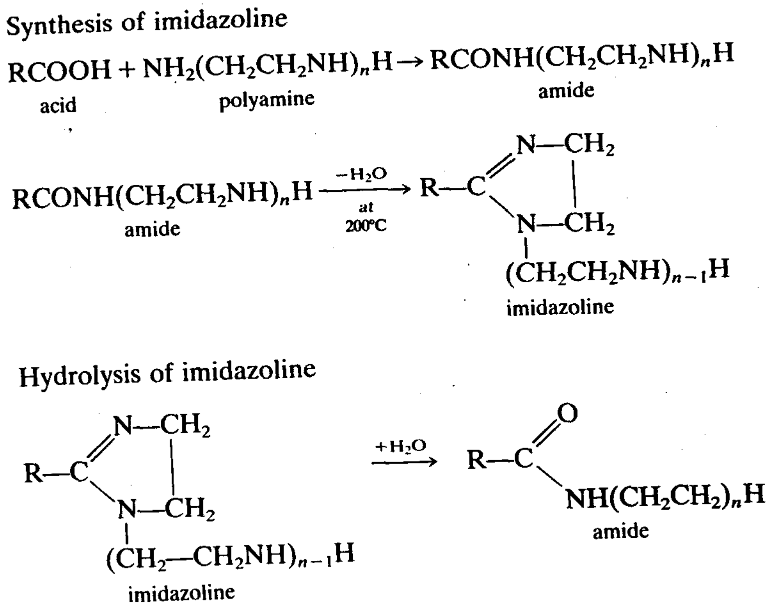
1. Amines, diamines, amides, amine salts, ethoxylated amines and imidazolines are used but the alkyl group tends to be C_{16}–C_{18}, making the products more oil soluble.[21]
2. Quaternaries are not normally used as corrosion inhibitors. The charge on a quaternary nitrogen is such that the products are generally water soluble unless two or more C_{18} alkyl chains are present. However, there are no absolute rules as quaternaries are also efficient bactericides in reducing or controlling sulphate reducing bacteria and so are often used as minor components in blends.

The composition of nitrogen based corrosion inhibitors is inadequately described in most of the literature on corrosion inhibition. This is due not only to secrecy but also to the fact that the composition of some of the more popular products is in some doubt. Practically all commercial surfactants used as corrosion inhibitors are mixtures rather than pure chemicals. The hydrophobic group is invariably a mixture of chain lengths, and products described as having a C_{12} alkyl chain could have appreciable amounts of C_{10} and C_{14} alkyl chains and smaller amounts of C_8 and C_{16}. In practice it has been found that such mixtures are often more efficient, particularly over a range of applications. In addition, products with amine and sulphonate polar groups can accurately represent more than 90% of the composition, but other product groups, namely alkanolamides and imidazolines, can have large amounts of other polar groups present. Imidazolines are used very frequently in oil/water systems and recently Martin and Valone[22] chemically examined the compositions of well known commercial corrosion inhibitors of the imidazoline type, viz.

Imidazoline + (Dimer/Trimer acid) + Surfactant + Solvent

It was shown that the imidazoline ring had hydrolysed back to the intermediate amide (Fig. 6.14).

This work showed that complete conversion of the imidazoline to the amide had occurred in about six weeks. Experiments were also carried out comparing formulated products that had been made from imidazoline, which had reacted with formulations where amide had been blended in place of the hydrolysed imidazoline. The corrosion inhibition results were the same, suggesting that it is the amide which is the active species.


Synthesis of imidazoline

$$RCOOH + NH_2(CH_2CH_2NH)_nH \rightarrow RCONH(CH_2CH_2NH)_nH$$

Hydrolysis of imidazoline

Fig. 6.14 Composition of imidazolines.

There is another possibility not mentioned in the above reference and that is the possibility of reaction between the dimer–trimer acid and the alkanolamide. In cold or warm conditions any reaction between the alkanolamide (which will contain free base) and the dimer–trimer acid will be an acid–base neutralisation. However, if the alkanolamide and the dimer–trimer acid are heated to a high temperature there is a distinct possibility of transamidation taking place. This example shows the chemical complexity of some corrosion inhibitors and the difficulty of relating chemical structure to inhibitor efficiency.

The laboratory testing of metal corrosion in an oil/water liquid phase with carbon dioxide or hydrogen sulphide present (to simulate crude recovery) is beset with problems. The most generally accepted is the 'wheel test'.[23]

6.5.2 *Cutting oils*

A familiar application of corrosion inhibition is that of soluble cutting oils where the medium is predominantly water with a low concentration of oil which both helps to lubricate and protect the fresh metal from corrosion. The products used in practice are concentrates of: mineral oil, boundary lubricants, emulsifier, corrosion inhibitor, bactericides, coupling agents, and defoamer.

This concentrate is diluted with mineral oil and then with water to about 5% active. Such products are known as soluble oils and appear as milk like oil in water emulsions. Such emulsions are quite stable for their period of use, but will separate out. However, if the concentrate is diluted with oil such that the emulsifier/oil ratio is much higher than the soluble oils, then on dilution with water (to 5% active) instead of a milk like emulsion a translucent or even transparent emulsion can be obtained. The emulsifier and corrosion inhibitors are of the same type in both the milky emulsions and the translucent emulsions, but their concentration relative to that of the oil is quite different. The translucent emulsions are known as microemulsions and are stable indefinitely. The composition of the microemulsions is still under debate but the current view is that the oil is contained inside the swollen micelles.[5,24]

The emulsifiers used in soluble cutting oils are petroleum sulphonates of mol. wt 425–480, potassium oleate (C_{18} unsaturated alkyl chain) and alkanolamide soaps based on C_{18} alkyl chain fatty acids. All these products are oil soluble and similar, but not identical to the corrosion inhibitors used in oil/water systems in oil field applications. The corrosion inhibitors are dimer acids (C_{10}), sodium nitrite, arylsulphonamide carboxylic acids and benztriazole. Thus, the corrosion inhibitors are not 'surfactants' with hydrophobic and polar groups. However, the emulsifiers, which are surfactants, play an important role in the corrosion inhibition in that the wrong choice of emulsifier can adversely affect corrosion inhibition. Thus, petroleum sulphonates of lower molecular weight may make excellent emulsions, but corrosion resistance decreases. Whether the emulsifiers act as film formers and thereby inhibit corrosion and/or act as wetting agents for the oil to wet the metal is not clear. Formulations of cutting oils are rarely published in detail, but more than one surfactant is normally employed.[25] It has been shown[5] that mixtures of surfactants often go through minima of interfacial tension with oil-in-water systems and this may account for the synergism observed in such systems.

6.6 Corrosion inhibitors used in nonaqueous systems

If water is completely excluded from the environment then no corrosion will take place. There are many examples of nonaqueous systems where water ideally should not be present, but in practice invariably occurs although in small quantities. Two applications where film forming corrosion inhibitors are used in nonaqueous systems are temporary rust preventatives and lubricating/hydraulic oils.

6.6.1 *Temporary rust preventatives*

Normally there are four components in a temporary rust preventative:

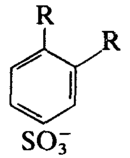
1. A film former, e.g. mineral oil, wax, bitumen.
2. A film forming corrosion inhibitor.
3. A water displacing additive.
4. A solvent.

The nature of the film former will determine the character of the film, e.g. bitumen will give a hard film, and mineral oil will give a liquid film.

The most widely used film forming corrosion inhibitors are the oil soluble sulphonates; these can be natural petroleum sulphonates or synthetic products. Petroleum sulphonates of mol. wt 500–600 are used as corrosion inhibitors. Many synthetic sulphonates have been developed as replacement for the petroleum sulphonates, the common feature being a hydrophobic group large enough to give oil solubility to the sulphonate. Whereas the sodium salt of the petroleum sulphonate is used as an emulsifier in cutting oils it is the barium and zinc salts which are used as corrosion inhibitors. Some typical synthetic sulphonates are shown in Fig. 6.15.

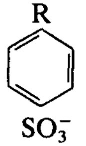
The next most widely used corrosion inhibitors are those with a carboxyl group, acids or esters. Tallow based soaps (with an alkyl chain of C_{18}) have been used for a long time as a component for corrosion inhibition, but the hydrophobic group must be larger than C_{18} to give good oil solubility. Dimer–trimer acids made from unsaturated fatty acids will give the required oil solubility and corrosion inhibition. The oxidation reaction products of mineral oil and waxes will give 'oxidates' which are products containing alcohols, esters, acids, lactones, aldehydes and ketones.

Dialkyl benzenesulphonates



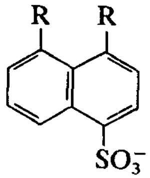
$R = C_{10}–C_{14}$ alkyl

Alkylbenzenesulphonates



$R = C_{22}–C_{26}$ alkyl

Dinonyl naphthalenesulphonates



$R = C_9H_{19}$ alkyl

Fig. 6.15 Oil soluble synthetic sulphonates.

Metal surfaces treated with temporary rust protectives are often wet with water, which must be removed and the surface wet with oil or wax. This is the function of the water displacing additive, which is usually a low molecular weight glycol, but is normally used in conjunction with a surfactant which readily forms 'reverse micelles' (see Fig. 6.13). The corrosion inhibitors will form reverse micelles, but they will have a limited capacity to solubilise water in the micelles.

There are applications of temporary corrosion inhibitors where water must be removed from the metal surface and then not solubilised into the solvent system, but rather be separated from the system by a phase separator so enabling the solvent solution to be reused on fresh wet metal. In this case the corrosion inhibitor must also function as a demulsifier, and surfactants with large bulky hydrophobic groups and a small hydrophilic group have been found to work extremely efficiently. One example is dinonylnaphthalene sulphonate (see Fig. 6.15).

A typical formulation for a temporary corrosion inhibitor giving a liquid film and capable of dewatering metal surfaces is:

Mineral oil	5%
Petroleum oxidate ester	5%
Petroleum sulphonate (barium salt)	5%
Dewatering pack	2%
Solvent	to 100%

The petroleum oxidate ester is obtained by esterifying a petroleum oxidate with a long chain alcohol. The dewatering pack would consist of low molecular weight glycols and sodium dioctyl sulphosuccinate.

6.7 Synergism in corrosion inhibition

There are numerous examples where synergy is mentioned in connection with corrosion inhibition, with most of the information in patent literature (e.g. Refs 26–29). One published paper, by Warner and Ward,[30] is of considerable interest in the synergism between dinonyl naphthalene sulphonate and organic acids in gas turbine lubricants. Similar synergism has been observed, in temporary rust protectives, between oil soluble sulphonates and oxidates from petroleum.

The explanation for the synergistic effects in film forming corrosion inhibitors is not clear at the present time. However, the most likely mechanism would seem to be in the coadsorption of different molecules on the surface which may pack or form a more coherent film than one product on its own. Another explanation could be that two dissimilar surfactants can form mixed micelles which have distinctly different properties to those of the individual components. The current ideas on the structure of microemulsions postulate that low molecular weight alcohols having a small cross-sectional area can pack in between surfactant molecules of much larger cross-sectional area and give high density packed interfacial layers. Similar packed layers of mixtures of surfactants could give improved resistance to corrosion, but there is no experimental evidence at present to support this idea.

6.8 Acknowledgements

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