Chapter Thirty-six

Preservatives

Introduction

Many of the materials used in the manufacture of toilet preparations are susceptible to biological degradation by micro-organisms. In this chapter methods of combating biodeterioration of products will be discussed.

In the past the contribution of the microbiologist to the cosmetics industry was considered of minimal importance.[1] More recently there has been an increasing awareness of the problems of microbial spoilage of cosmetic and toiletry products. Formerly the emphasis was placed on loss of aesthetic appeal of the product with a consequential loss of profitability, while the health hazard to the consumer was largely ignored. Since micro-organisms are ubiquitous, the body is continually exposed to them and it therefore seemed unnecessary for toilet preparations to be sterile. Although it was accepted that products should not constitute any greater microbial hazard than that presented by the normal environment, little was done to show that this was achieved.

Normally healthy individuals have considerable resistance to infection by bacteria and fungi commonly found on their skin and in their usual environment, but in susceptible individuals, for example the newborn, the very old, those in ill health or under drug therapy, there is an increased probability of infection developing. It should be remembered that a product may contain a growing bacterial population even though there is no visible evidence of this. Such a product placed in intimate contact with the skin, particularly if it is broken or damaged, may give rise to infection.[2] Examples in the literature which demonstrate the importance of considering the possible health hazard of a contaminated product will be discussed later.

Preservatives are, therefore, added to products for two reasons: firstly to prevent spoilage, that is, to prolong the shelf-life of the product, and secondly to protect the consumer from the possibility of infection.[3] It is recognized that products may require protection from contamination during manufacture, although preservation must never be used to hide bad manufacturing procedures.[4] Duke[3] quotes examples illustrating how products containing preservatives can be microbiologically unacceptable because of bad manufacturing practice. It is also recognized that cosmetic products, possibly more so than pharmaceutical products, are liable to consumer abuse. Although products cannot be protected against extremes of abuse, such as the use of saliva in the application of eye make-up, the manufacturer should anticipate misuse when the product is formulated.[3]

It is therefore imperative that the microbiologist be involved in the formulation of a product from its development stage onwards.[5] It can no longer be assumed that a manufacturer has fulfilled his obligation to the consumer if the product in question leaves his premises in a microbiologically satisfactory condition. If, however, products are to be expected to remain resistant to the introduction of extraneous micro-organisms during their period of use, this will impose a greater strain on the preservative system chosen and will make it even more important for manufacturers to carry out thorough and realistic tests both during the development of new products and in the production and quality control of existing lines.

The Council of the British Society of Cosmetic Chemists has published a monograph on the hygienic manufacture and preservation of toiletries and cosmetics.[6] Further indications of the importance currently attached to ensuring the adequate preservation of all toilet preparations and cosmetics are evident in the number of investigations into contaminated preparations and the possible clinical significance of contamination. Some of these reports are discussed later in the chapter.

Microbial Metabolism

Micro-organisms grow and multiply by utilizing the materials in their immediate environment. In considering spoilage problems created by micro-organisms, the variety of chemical reactions they can carry out and the rate at which these can occur must be taken into account.

Bacteria and fungi are widely distributed in nature and there are few places on or near the surface of the earth that are free from them. They occur, for example, in such unlikely places as hot mineral springs, the effluents from gas works, stagnant salt lakes and even in the essentially anhydrous environment of diesel fuel. The only places where micro-organisms are not found are those in which a sterilizing influence prevails or in the interior tissues of healthy animals and plants. In growing, bacteria and fungi can cause rapid and profound changes in their immediate environment and in the synthesis of new protoplasm many complex chemical reactions are accomplished within a remarkably short period of time. The organisms carry out these reactions by means of enzymes and some of the basic reactions that can occur are as follows:

Hydrolysis	The addition of H_2O to the molecule. The next step in molecular breakdown is often thus facilitated so that molecules are split at the hydrolysed link.
Dehydration	The removal of H_2O from one or more molecules.
Oxidation	The removal of hydrogen or the addition of oxygen to the molecule; also a process which involves an increase in the number of positive charges on an atom, or a decrease in a number of negative charges.
Reduction	The removal of oxygen or the addition of hydrogen; the reverse reactions to those of oxidation.
Decarboxylation	The removal of CO_2.
Deamination	The removal of $—NH_2$.

Phosphorylation	The esterification of the molecule with phosphoric acid. This is usually accomplished by the transfer of the phosphate radical from some substance other than phosphoric acid itself.
Dephosphorylation	The removal or hydrolysis of phosphoric acid from phosphorylated compounds.

In a product supporting the growth of different kinds of micro-organisms a large variety of end products will be produced, and in mixed populations there is, of course, a certain amount of competition for essential nutrients between the different organisms. Those that can convert the environment satisfactorily survive, while those which only live with difficulty die out, providing a further source of convertible substrate for those that remain. In utilizing the substrate, the metabolic processes of some organisms result in the formation of acid end products which have a limiting effect on growth, and in some cases the changes brought about are sufficient to inhibit further growth. Most organisms are, however, capable of carrying out neutralizing reactions and in this way some degree of stabilization of the environment can be achieved.

The speed with which micro-organisms can propagate, and the variety of reactions which they can accomplish, indicate how necessary it is to inhibit their growth in products whose physical characteristics must remain unchanged during long periods of storage and use in the hands of the consumer.

The manifestations and mechanisms of microbial spoilage have been discussed by Smart and Spooner.[7] Microbial contamination may be made apparent by visible growth of the contaminant. For example, moulds and fungi frequently can be detected as they grow macroscopically, usually on the surface of the product or the lining of the pack. Micro-organisms may also be visible in liquid preparations as turbidity or sedimentation. Colour changes may occur as a result of alterations in pH or redox potential or because of pigment production by the contaminating organism, for example the blue-green to brown pigments produced by *Pseudomonas* genus.

The metabolic processes of some organisms cause the formation of gas which may be seen as bubbles or frothing in liquid preparations. Frequently spoilage is indicated by odour productions. In addition, micro-organisms may cause cracking of emulsions, alterations in rheological properties or loss of texture in topical preparations. Although direct evidence is lacking, spoilage may be detected as an allergic reaction to the application of foreign protein to the skin from a heavily contaminated product.

All these effects can be brought about quite quickly if large numbers of organisms are present or if the product possesses properties which favour rapid multiplication. Inadequate preservation may, however, only reveal itself after many months if the conditions are such that growth can only take place after the organisms have adapted themselves to the environment. The process of adaptation may involve gradual alteration of pH by the organism to a level at which growth can take place at a greater speed, or may necessitate the use of metabolic processes not normally employed by the organism under optimum conditions.[8] It may also involve development of increased resistance to, or metabolism of, the preservative. *Pseudomonas* species have been found to develop total resistance to parabens and benzalkonium chloride, used as preservatives in detergent-containing products. In both products the *Pseudomonas* was found to metabolize the detergent.[9] The contamination of a product with *Cladosporium resinae* was discovered to occur as a result of the ability of this fungus to hydrolyse the preservative methyl parabens to *p*-hydroxybenzoic acid.[10]

Clinical Significance of Contamination

A number of independent surveys have been conducted on the type and extent of contamination in used and unused cosmetics (see Table 36.1, Baker,[11] Ahearn and Wilson[20]). Table 36.2 lists some of the genera of micro-organisms which have been isolated from cosmetic and toiletry preparations. Gram-negative organisms, in particular the pseudomonads, seem to be the most frequently isolated organisms in unused cosmetics. Used cosmetics are most frequently contaminated with staphylococci, diphtheroids, micrococci, fungi and yeasts. While it is appreciated that contaminated cosmetics may lose their aesthetic appeal, less is known about the potential danger of these contaminants to the consumer. Certain cosmetic preparations, such as hand creams and lotions, are extensively used in hospitals; because patients are more likely to be susceptible to infections than healthy individuals, the microbial state of these cosmetics may have important implications. Perhaps the most striking example of this was the investigation by Morse *et al.* [21] of a septicaemia outbreak caused by *Klebsiella pneumoniae* in a hospital intensive care unit, the source of which was found to be a dispensing bottle of contaminated lanolin hand cream. These workers in a later survey[22] within a particular hospital examined 26 brands of hand cream, used and unused. Four brands were found to contain a variety of Gram-negative bacteria and it was suggested that the increase in numbers of Gram-negative infections in this hospital was related to the use of contaminated products.

There is increasing evidence implicating contaminated cosmetics in the production or persistence of eye infections. Ocular cosmetics become contaminated with resident bacterial flora from the skin and eyes, plus animal-associated yeasts and saprophytic moulds. These organisms may grow in the cosmetics and be inoculated in high numbers into the outer eye.[14,17] A correlation between organisms found in the outer eye and those found in the cosmetics of the user has been shown.[14] In one case an association between contaminated mascara and keratomycosis was demonstrated, the causative fungus, *Fusarium solani*, being isolated from the mascara. In another case *Staphylococcus aureus* was isolated from the eyelid margins of a woman with blepharitis and from the mascara which she was using daily, thus perpetuating the condition. Other observations indicated that potential eye pathogens can establish themselves in a cosmetic within a week with only moderate use.[17] Ahearn *et al.*[20] were able to correlate use of contaminated cosmetics with four cases of staphylococcal blepharitis or conjunctivitis when the conditions were cured by withdrawal of the cosmetic.

Since new eye cosmetics are less frequently contaminated with fungi or bacteria, it appears that contamination of the product by the user is the principal problem.[14]

Table 36.1 Summary of Some Investigations into P Contamination

Products	Used/ Unused	Contaminated (%)	Organisms Most Frequency Isolated	Source
250 products covering wide range	Unused	24·4	*Pseudomonas* species and other Gram-negative rods. Most frequently contaminated products were hand and body lotions, liquid eye liners and cake eye shadows.	Wolven and Levenstein (1969)[12]
169 hand and body lotions and creams	Unused	19·5	*Pseudomonas* species and other Gram-negative rods.	Dunnigan and Evans (1970)[13]
428 eye cosmetics	Used	12	Fungi—mainly *Penicillium* and *Cladosporium*, and yeasts—mainly *Rhodotorula rubra* and *Candida parapsilosis*.	Wilson *et al.* (1971)[14]
		43	Bacteria—mainly Gram-positive micrococci. 17 products contained Gram-negative rods, 6 of which were *Pseudomonas aeruginosa*.	
58 eye cosmetics	Unused	3·4	Gram-negative rods, one of which was *Escherichia coli*.	
223 products covering wide range	Unused	3·5	*Pseudomonas* species and other Gram-negative rods.	Wolven and Levenstein (1972)[15]
165 products covering wide range, of which 23 were eye cosmetics	Unused	12	Diphtheroids, staphylococci and aerobic spore-forming bacilli. None of the eye cosmetics were contaminated.	

Table 36.1 (*cont.*)

Products	Used/ Unused	Contaminated (%)	Organisms Most Frequency Isolated	Source
222 products covering wide range, of which 79 were eye cosmetics	Used	49	Staphylococci. 35 per cent of the eye cosmetics were contaminated. For both used and unused cosmetics, Gram-negative bacilli were isolated from an insignificant number of products.	Myers and **Pasutto** (1973)[16]
19 medicated cosmetics	Used	52	Staphylococci. Indicates that contamination is possible even in products with high concentrations of antimicrobial agents.	
29 applicators	Unused	27·5	Staphylococci and diphtheroids.	
37 applicators	Used	100	Staphylococci.	
200 mascaras	Unused	1·5	—	Ahearn *et al.* (1974)[17]
	Used	60	Most common bacteria were *Staphylococcus epidermidis* and *Micrococcus* species. Most common fungi and yeasts were *C. parapsilosis* and *Cladosporium* species.	
172 products covering wide range	Unused	<50	Gram-negative rods. Most heavily contaminated products were specific brands of eye make-up (especially liquid eyeliner), bath detergent and complete make-up.	Jarvis *et al.* (1974)[18]
147 products covering wide range	Unused	32·7	Principally aerobic spore-bearers and Gram-positive cocci, but Gram-negative rods, in particular the pseudomonads, also isolated.	Baird (1977)[19]

Table 36.2 Some Micro-organisms Isolated From Toilet Preparations

Fungi	Bacteria	Yeasts
Absidia	Acinetobacter	Candida*
Alternaria*	Alcaligenes	Monilia
Aspergillus*	Bacillus*	Torula
Citromyces	Diphtheroids	Zygosaccharomyces
Cladosporium*	Enterobacter	
Dematium	Enterococcus	
Fusarium	Escherichia	
Geotrichum	Klebsiella*	
Helminthosporium	Micrococcus	
Hormodendrum	Proteus	
Mucor*	Pseudomonas*	
Paecilomyces	Sarcinia	
Penicillium*	Serratia	
Phoma	Staphylococcus*	
Pullularia	Streptococcus*	
Rhizophus*		
Stemphylium		
Trichothecium		
Verticillium		

* Several different species of these genera have been reported.

Origins of Contamination

Raw Materials

If the raw materials used in manufacturing of cosmetics are heavily contaminated then it is almost inevitable that the finished product will be similarly contaminated, and any preservative system present will be unnecessarily can be avoided by careful monitoring of raw materials.

The water used in product manufacture is possibly the most frequent source of contamination, often supporting large numbers of micro-organisms. Mains water contains low numbers of organisms, usually less than 300 ml^{-1}. Softened, distilled or, in particular, deionized water is capable of supporting the growth of some bacteria, and numbers can rise to 10^6–10^7 ml^{-1} when water is stored.[23–25] Storage tanks are thus frequently responsible; Baker[11] describes several cases of serious product deterioration which were traced to heavy contamination in the beds of ion exchangers or water tanks. More recently Duke[3] describes the contamination of a hair rinse with waterborne Gram-negative organisms which were using cetrimide in the product as a nutrient. Correlations between shampoo spoilage and waterborne organisms have been discussed.[26]

Fats, waxes and refined oils contain relatively few organisms whereas natural materials such as gums and herbs are frequently very heavily contaminated by a variety of fungi, yeasts and bacteria. The natural gums, tragacanth, karaya and acacia, are always very heavily contaminated; the synthetic gums are often almost sterile. Other naturally occurring materials such as talc, kaolin, chalk and rice starch frequently carry large numbers of bacteria, particularly those that are capable of forming spores. Duke[3] reports contamination of a face preparation by a pigment contaminated with bacteria. The contaminants were killed by addition of a preservative.

The containers of raw materials—drums, sacks, cartons, etc.—may also be a source of contamination prior to manufacture.

Environment

A further possible source of contamination is the air, which contains mainly mould and bacterial spores and skin cocci. Environmental control is facilitated by covering of containers and reduction of air-currents over a product.[23] Routine monitoring of the air and selected surface sites within the production area is advised, so that deviations from normal standards of cleanliness are immediately detected.[1]

A survey of the types of organisms found in manufacturing environments and how these varied over a nine-month period has been conducted by Bruch.[27]

Equipment

During manufacture the product can easily become contaminated by organisms which accumulate in the plant as a result of faulty or inadequate cleansing. Pieces of equipment with inaccessible joints, pipes and pumps are often difficult to clean properly and washing with detergent solutions may only result in dilution of the product to form stagnant foci where bacteria and fungi thrive. Plant should be designed to facilitate easy cleaning and disinfection, and inaccessible grooves and dead-ends in all items which come into contact with the product should be avoided wherever possible (see Chapter 43).

An example of product deterioration resulting from plant contamination is given by Duke.[3] A broken sealing joint in a bulk tank used for the manufacture of a shampoo allowed shampoo and contaminated cleansing water to enter a false bottom of the tank. As the preservative had been diluted, the contaminants survived and were washed into each new batch of shampoo. Using the shampoo base as nutrient, the bacteria then contaminated the whole product.

The need for good housekeeping procedures cannot be stressed too strongly. Of paramount importance is the education of plant operatives to appreciate the necessity of properly performed plant cleaning operations.

Advice on methods of plant cleaning and disinfection are given by Davis[28] who states that 150–200 ppm of hypochlorite will sanitize clean metal and glass in two minutes and sterilize in 10 minutes. The corrosive nature of this treatment is a disadvantage and formaldehyde is frequently used in preference. Hot water, or preferably live steam, has been recommended as the best disinfecting agent.[23] Detergent sanitizers containing quaternary ammonium compounds or detergent–iodine mixtures are also useful, but it is essential to remove product residue from the plant and to rinse thoroughly with hot water before utilizing any of the above disinfection procedures since many are inactivated by residues of organic material. Air locks in the plant may also prevent certain parts coming into contact with the cleaning and sterilizing fluids and should be avoided.

Microbiological tests should be made on equipment and filling lines before and after sanitization to ascertain the effectiveness of cleaning procedures. RODAC plates and swabbing techniques may be used for this purpose together with sampling of the final rinse fluid after sanitization to determine the cleanliness of internal surfaces.[1]

Packaging Materials

Since most products are exposed to further contamination during filling into containers, cleaning and disinfection of filling equipment is also important (see Chapter 43). Containers and closures should be dust-free and microbiologically clean. This can be achieved by a filtered air blast which is probably more effective than the use of detergent and water.[23] Caps and liners are notorious for an abundant fungal flora and much of the growth on the surface of cosmetic creams is directly attributable to cap linings. Quite frequently creams containing preservatives, which are otherwise adequately preserved, break down following the introduction of large numbers of fungal spores from a cap lining. These organisms germinate initially in the microfilm of water on the lining and spread gradually to areas of slight separation around the edge of the cream. Many toilet preparations, in addition to having a long shelf-life, may be in use by the consumer for many months, so that spoilage does not become apparent until the contents are more than half used. Products packed in wide mouthed jars, and flexible bottles which draw air back into them, are more liable to contamination than those packed in collapsible tubes and bottles with small orifices.

As plastic materials are not subject to biodegradation, use of such materials instead of cellulosic materials should be associated with a reduction in microbial spoilage. Unlike paper, card and cork, plastics are microbiologically pure but as they are porous to oxygen and carbon dioxide and encourage water condensation, spoilage by mould spores will be facilitated.[7]

Personnel

Probably the greatest microbial hazard to the product during manufacture or packaging is from the operators.[23,29] Operators should be properly instructed to appreciate that they are a potential source of contamination and trained to maintain high standards of personal hygiene and cleanliness. The wearing of protective overgarments is advisable.[23]

Microbial Growth in Products

A number of factors determine whether micro-organisms will survive and propagate in a product and hence these influence the need for preservation. Some of the more important are examined below.

Water Content

Because micro-organisms depend on water for the synthesis of cellular components, the physical and chemical characteristics of the water phase in an emulsion, for example, are dominant factors in determining whether growth occurs. In single-phase non-emulsion products, however, the amount of growth that will occur is determined by the pH, osmotic pressure, surface tension and oxygen tension of the system.

In general, emulsions with a water-continuous phase are more susceptible to bacterial attack than those with an oil-continuous phase although bacteria have frequently been isolated from inadequately preserved water-in-oil emulsions. Until fairly recently it was presumed that micro-organisms would only survive in aqueous environments but De Gray and Killian[30] stated that certain bacteria and fungi could survive for extended periods of time in hydrocarbons free of any separate aqueous phase. In addition, anhydrous cosmetic products have been shown to support the growth of contaminating micro-organisms.[17] In this instance it was suggested that moisture had entered the products either via the user or through condensation. In emulsions there is likely to be migration of organisms from the oil phase to the water phase and since the oil phase may not be entirely anhydrous, migration in the opposite direction cannot be ruled out. Some micro-organisms are able to degrade triglycerides in emulsions, a process which is facilitated by the marked adsorption of organisms at the oil–water interface. Fatty acids and glycerol are liberated, which can then be metabolized for growth purposes.[31] Bennett,[32] in a study of the preservation of emulsions, found that the oil-to-water ratio had a significant effect upon the magnitude of growth. Equal numbers of *Pseudomonas aeruginosa* cells were inoculated into a series of emulsions with different oil-to-water ratios and it was found that the amount of growth increased with the increase in water content.

The nutritive value of the aqueous phase of any product will contribute to the amount of growth that will occur and the presence of such materials as carbohydrates, proteins and, for example, phospholipids will increase the need for adequate preservation. Sorbitol, glycerol and even surface-active agents (particularly the nonionics, but also to a lesser extent anionics) when present at low concentrations can all be metabolized by micro-organisms. Barr and Tice[33] reported the splitting of the ester linkages of certain nonionic surfactants by *Pseudomonas aeruginosa*, *Aspergillus niger*, *Penicillium notatum* and *Monilia albicans*. Their results indicated that the organisms were capable of growing in the surfactant esters and splitting them and that the rate of growth and ester splitting was dependent on the number of organisms in the inoculum. Anionic surfactants are also capable of acting as sources of energy for micro-organisms. Their chemical structure controls their susceptibility to attack and certain bacteria are capable of oxidizing terminal methyl groups to carboxyl groups. According to Sawyer and Ryckman[34] the alkyl sulphates, sulphonated fatty acids, amides and esters, and the low-molecular-weight polyethylene glycol derivatives are rapidly broken down, while the alkyl aryl sulphonates, alkyl phenoxypolyoxyethanols and high-molecular-weight polyethylene glycol derivatives are attacked more slowly. Yu-Chih Hsu[35] discovered six strains of *Pseudomonas* which were capable of splitting sodium alkyl sulphates.

The nutritive value of many vegetable gums utilized as thickeners is also well known. Polysaccharides may be attacked by extracellular enzymes and thus depolymerized. Starch may be degraded by amylases and carboxymethylcelluloses by cellulases. It has been reported that, of the range of celluloses available, the most resistant to attack are methyl- and ethyl-celluloses.[31]

pH Value

The pH value of a product will affect the degree of ionization of utilizable materials, influence the electrical charge at the bacterial and fungal cell walls, determine enzyme production and activity and hence regulate the availability of nutrients and the ease with which they are assimilated by the microbial cell. However, since growth tolerance limits for pH differ widely for various micro-organisms, pH itself should never be regarded as a factor likely to contribute to self-sterilization of a product. *Pseudomonas* species, which are extremely common contaminants of toilet preparations, can exist over as wide a pH range as 3·0–11·0 and although many fungi grow most prolifically at acid pH they have been known to survive on vanishing creams at pH 9.

Osmotic Pressure

The living semi-permeable membranes which surround the bodies of all micro-organisms can be ruptured by changes in osmotic pressure and this can lead to membrane shrinkage and dehydration of the organism. For this reason osmotic pressure can have a limiting effect on growth. Concentrations of between 40 and 50 per cent of glycerin and sorbitol are inhibitory to micro-organisms by reason of the osmotic pressure, and high concentrations of electrolytes can exert a similar limiting action. Thus very concentrated products are likely to be self-preserving but those which may be diluted and left standing before use can deteriorate if left for periods of several days. Shampoos, for example, which are frequently sold to professional hairdressers as concentrates for dilution before use, are often susceptible to bacterial degradation as the concentrates may be diluted with contaminated water and left uncovered for long periods during use.

Surface Tension and Oxygen Tension

Quite apart from the nutritive value of low concentrations of some surfactant molecules, surface tension is itself a factor influencing growth. Many Gram-negative bacteria, and the coliforms in particular, grow well in environments abounding in surfactants, while most Gram-positive organisms do not grow well at surface tension levels much below 50 dyn/cm (0·05 N/m). Gram-negative organisms, particularly the pseudomonads, flourish in shampoos and are also common contaminants of the aqueous phases of emulsions. Cationic surfactants are toxic to many organisms, anionics to a few, and nonionics to hardly any; thus surface tension *per se* will not be a gross limiting factor but will have an effect in association with the presence or absence of toxic groups in the surfactant molecules. Most organisms, bacteria and fungi which contribute to product spoilage are aerobic and depend on the availability of oxygen for their metabolism. The microclimate in most products, with perhaps the exception of those in pressurized packs, will almost invariably provide sufficient oxygen for the growth of micro-organisms provided that all other factors are favourable.

Antimicrobial Spectrum of the Preservative System

In a cosmetic, as in the natural environment, there is competition between organisms for nutrients so that one organism will survive and grow more successfully than others. Thus where a preservative is active against a limited spectrum of organisms, the product may be left open to spoilage by less susceptible organisms.[36]

Temperature

The susceptibility to microbial attack will vary with the temperature of storage, so that a cosmetic kept at room temperature will be liable to spoilage by different organisms from those that flourish in a product kept in a hot environment (for example one left in the sun or in a hot car). Bacteria generally prefer temperatures of 30°–37°C and fungi and yeasts 20°–25°C.[36]

Preservative Requirements

The 'ideal' preservative which is both safe and effective in all kinds of toilet preparations has not yet been discovered and this means that the composition of each new product must be studied in detail before selecting a suitable preservative. In order to avoid preservative failure a careful analysis must be made of the factors in the product that are likely to favour the growth of micro-organisms, the ingredients that are likely to be contaminated before use, and also those that are likely to influence adversely the efficiency of whatever preservative is ultimately selected. The essential requirements of a preservative are:

(i) freedom from toxic, irritant or sensitizing effects at the concentrations used on the skin, mucous membranes and, in the case of orally administered products, on the gastro-intestinal system;
(ii) stability to heat and prolonged storage;
(iii) freedom from gross incompatibility with other ingredients in the formula and with the packaging material, which could result in loss of antimicrobial action.

Other requirements are that the preservative should be active at low concentration; should retain its effectiveness over a wide range of pH; should be effective against a wide range of micro-organisms; should be readily soluble at its effective concentration; should have no odour or colour; should be non-volatile; should retain its activity in the presence of metallic salts of aluminium, zinc and iron; should be non-corrosive to collapsible metal tubes and non-injurious to rubber.

Table 36.3 lists some of the preservatives used in cosmetics and toilet preparations. Compounds closely related to those listed in Table 36.3 have also been used, and inspection of the variety of preservatives available shows that a thorough understanding of the factors that can influence the efficiency in a particular system is necessary before a selection can be made.

The properties of some individual preservatives have been discussed by Gucklhorn,[37] Rosen and Berke,[36] Croshaw[38] and Cowen and Steiger.[39] Table 36.4 indicates the advantages and disadvantages of some of the established groups of preservatives.

Factors Influencing the Effectiveness of Preservatives

Dissociation and pH

Formulations of cosmetics and toiletries encompass a wide pH range and since micro-organisms of one sort or another are capable of growing between pH 2 and pH 11, ideally a preservative should be effective over this range.[38] In

Table 36.3 Some Preservatives Used in Cosmetics and Toilet Preparations

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p-Hydroxybenzoic acid
Benzoic acid
Sorbic acid
Dehydroacetic acid
Formic acid
Salicylic acid
Boric acid
Vanillic acid
p-Chlorobenzoic acid
o-Chlorobenzoic acid
Propionic acid
Sulphurous acid
Trichlorphenylacetic acid

Methyl *p*-hydroxybenzoate
Ethyl *p*-hydroxybenzoate
Propyl *p*-hydroxybenzoate
Butyl *p*-hydroxybenzoate
Benzyl *p*-hydroxybenzoate

Benzethonium chloride
Benzalkonium chloride
Cetyltrimethyl ammonium bromide
Cetylpyridinium chloride
Dimethyldidodecenyl ammonium chloride
β-Phenoxy-ethyl-dimethyl-dodecyl ammonium bromide
Tetramethylthiuramdisulphide
1-(3-Chloroallyl)-3,5,7-triazonia-adamantane chloride
5-Bromo-5-nitro-1,3-dioxan
6-Acetoxy-2,4-dimethyl-*m*-dioxan
Imidazolidinyl urea
Vanillin
Ethyl vanillin

Phenol
Cresol
Chlorothymol
Methylchlorothymol
Chlorbutanol
o-Phenylphenol
Dichlorophene
Hexachlorophene
Parachlormetaxylenol
Parachlormetacresol
Dichlormetaxylenol
p-Chlorphenylpropanediol
β-Phenoxyethylalcohol
β-*p*-Chlorphenoxyethylalcohol
β-Phenoxypropylalcohol
Potassium hydroxyquinoline sulphate
8-Hydroxyquinoline
p-Chlorphenylglyceryl ether
Formaldehyde
Hexamine
Monomethylol dimethyl hydantoin
2-Bromo-2-nitro-1,3-propanediol
1,6-*Bis*-*p*-chlorophenyl diguanidohexane
Phenyl mercury acetate
Phenyl mercury borate
Phenyl mercury nitrate

Sodium ethyl mercurithiosalicylate
Tetrachlorsalicylanilide

Trichlorsalicylanilide
Trichlorcarbanilide

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practice many preservatives are pH-dependent, the majority of them being more active in the acidic than alkaline range. Some preservatives with a wide pH profile have the disadvantage of being chemically highly reactive compounds (for example formaldehyde and formaldehyde donors) which react with other components of the formulation.[39] pH may also have an effect on the microbial cell surface[40] and may affect the partitioning of an antimicrobial agent between the cell and the product.[41]

For many preservatives the most pronounced effect of pH on activity is on the antimicrobial agent itself. Many weak acids are used as preservatives, their activity depending upon the amount of undissociated acid, which in turn depends on the dissociation constant and pH of the system (see Tables 36.5 and 36.6). It has been suggested that anions of acids may be inactive as a result of

Table 36.4 Advantages and Disadvantages of Some Established Preservatives

Preservative	Advantages	Disadvantages
Alcohols, e.g. ethyl alcohol, isopropyl alcohol	Broad spectrum	Volatile High concentrations (15–20 per cent) required
Quaternary ammonium compounds	Better as active agents, e.g. in deodorants	Ineffective against some pseudomonads except at high concentrations which may be irritant Incompatible with proteins, anionics and nonionics
Acids, e.g. benzoic, sorbic, dehydroacetic	Active against fungi	pH-dependent because of dissociation
Formaldehyde	Broad spectrum Cheap Water-soluble Retains activity in presence of surfactants	Irritant (banned in some countries) Volatile Unpleasant odour Highly reactive chemically Incompatible with proteins
Parabens (*p*-hydroxybenzoates)	Low toxicity Relatively non-irritant at use concentrations Relatively effective over wide pH range	More active against fungi and Gram-positive bacteria than against Gram-negative bacteria Low water-solubility Partition in favour of the oily phase Inactivated by nonionics, proteins
Organic mercurials, e.g. phenyl mercuric salts	Broad spectrum Stable	High toxicity and irritancy Inactivated by proteins, anionics but to much less extent by nonionics Low water-solubility.
Phenolics	Useful as packaging preservatives and as active agents.	Low water-solubility Partition into the oil phase Volatile Incompatible with anionics above critical micelle concentration and with nonionics May be irritant

Data reproduced by kind permission of Miss B. Croshaw and *International Journal of Cosmetic Science.*[38]

Table 36.5 Dissociation Constants of Acids used as Preservatives

Preservative		Dissociation constant
Sulphurous acid	H_2SO_3	$1{\cdot}70 \times 10^{-2}$
o-Chlorobenzoic acid	*o*-Cl.C_6H_4COOH	$1{\cdot}20 \times 10^{-3}$
Salicylic acid	*o*-HO.C_6H_4COOH	$1{\cdot}06 \times 10^{-3}$
Formic acid	H.COOH	$1{\cdot}80 \times 10^{-4}$
p-Chlorbenzoic acid	*p*-Cl.C_6H_4COOH	$1{\cdot}05 \times 10^{-4}$
Benzoic acid	C_6H_5COOH	$6{\cdot}30 \times 10^{-5}$
p-Hydroxybenzoic acid	*p*-HO.C_6H_4COOH	$3{\cdot}00 \times 10^{-5}$
Sorbic acid	$CH_3CH{:}CHCH{:}CHCOOH$	$1{\cdot}73 \times 10^{-5}$
Propionic acid	C_2H_5COOH	$1{\cdot}40 \times 10^{-5}$
Dehydroacetic acid	$OCOCH(COCH_3)COCH{:}C(CH_3)$	$5{\cdot}30 \times 10^{-6}$

Table 36.6 Percentage of Preservative Undissociated Related to pH Value

Preservative	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7
Benzoic acid	99	94	60	13	1·5	0·15
Boric acid	100	100	100	100	100	100
Dehydroacetic acid	100	100	95	65	15·8	1·9
p-Chlorobenzoic acid	99	91	52	9·7	1·06	0·107
Propionic acid	100	99	88	42·0	6·7	0·71
Salicylic acid	90	49	8·6	0·94	0·094	0·0094
Sorbic acid	—	98	86	37	6·0	0·6

repulsion from the negatively charged microbial cell wall. Benzoic acid is an excellent preservative in its undissociated form but is strongly pH-dependent, so that at pH 6 approximately 60 times as much benzoic acid is required as at pH 3. Similarly, sorbic acid is present mainly in the undissociated (active) form at pH 4, but only 6 per cent of this form is present at pH 6. A chlorine addition product of sorbic acid[42] is claimed to be more effective than sorbic acid itself and less affected by high pH.

Dehydroacetic acid enolizes to give a weak acid and has been studied extensively as a preservative, particularly for foodstuffs.[43–45] It has a very low dissociation constant which indicates that it retains activity at higher pH values than most other organic acids and for this reason it commands wider usage. At pH 6, 16 per cent of the dehydroacetic acid is in its undissociated form, which is more than benzoic acid at pH 5. The anion of dehydroacetic acid is said to be weakly antimicrobial so that at pH 7 this acid will retain some activity.[36]

Phenols, which include the Parabens, behave as weak acids and consequently are less dramatically affected by pH than stronger acids. For example, methyl Paraben at pH 8.5 is approximately 50 per cent undissociated.

The relationships between pH and effectiveness of a range of preservatives have been studied by a number of workers.[46–48] Simon[48] showed that the biological activity of weak acids is influenced in a regular manner by changes in pH; in a study of 90 pH experiments involving a wide range of acids and test organisms he showed that the relationship between pH and activity is quite general for this type of preservative. When the pH of the environment is below the pK_a, changes of pH are of little consequence, but as the pH is increased above the pK_a higher concentrations are required to produce a standard response.

Other preservatives, for example cationics, are active only in the ionized form. Activity of cetrimide increases with pH as a result of increased cellular uptake.[49] Quaternary ammonium compounds are active at alkaline pH, but activity is progressively lost at lower pH values.[39]

Some preservatives are pH-dependent by virtue of their chemical instability. For example, 2-nitro-2-bromo-propanediol (Bronopol) loses activity as a result of degradation above pH 7 more rapidly than at pH 4. On the other hand hexamethylene tetramine is stable and inactive above pH 7 since it relies on chemical breakdown with the production of formaldehyde for antimicrobial action.[39]

Cowen and Steiger[39] give the optimum pH range for a number of preservatives.

In order to utilize a preservative economically and effectively it is necessary to know whether there is a correlation between pH and activity. If this aspect of formulation had been studied more closely in the past, a great deal of money could have been saved by the many manufacturers who used preservatives which could not be effective under the pH conditions prevailing in their products.

Concentration of Preservative

There cannot be any hard and fast rules about the optimum concentrations at which various preservatives should be used. This will be obvious from the foregoing paragraphs which mention the multitude of factors that contribute to the growth of organisms in products and the effectiveness of preservatives in those environments. Some products, by virtue of the concentration of materials in their aqueous phase, are virtually self-preserving without any addition of preservatives being necessary, whereas others may provide a nutritious environment for the growth of micro-organisms and thus require a fairly high concentration of a powerful preservative.

Effective concentrations of preservatives range from as little as 0·001 per cent in the case of organic mercurial compounds to 0·5 per cent or even 1 per cent of such materials as the weak acids, depending on the pH of the product.

The availability of the preservative to the micro-organisms it is required to inhibit is probably more important than the overall concentration itself. 'Availability' in this context can be defined in accordance with the mechanism of action of the particular preservative, and may depend on the permeability across the cell wall (if this is the mechanism), the flux (if diffusion rate is important) or degree of adsorption (if the preservative acts by coating the surface of the organism). The availability of the preservative is also influenced by the distribution, or partition, of the preservative between phases of the product. Partitioning properties of preservatives are discussed later in the chapter.

There are certain advantages in using preservatives in combination rather than singly, which are as follows: (a) a broadening of the antimicrobial spectrum of activity; (b) the use of a lower concentration of each of the preservatives, thus avoiding problems of toxicity or insolubility; (c) a reduced probability of survival of an organism resistant to one of the preservatives, provided that the other preservative(s) in the system act by a different mechanism; (d) the antimicrobial activity of the combination may be greater than the additive effects of the individual preservatives.

Frequently the esters of *p*-hydroxybenzoate are used in combination, the methyl ester in the aqueous phase of an emulsion and the propyl ester in the oil phase. Addition of the preservative to the oil phase is not so much to prevent the multiplication of organisms in this phase, as this seldom occurs, but to prevent diffusion or partition of the methyl ester from the aqueous phase into the oil phase; the presence of propyl ester in the oil phase will tend to stabilize the distribution between the phases. Bean *et al.*[50] have examined the activity of phenol against *E.coli* in oil–water dispersions and determined the distribution of phenol between oil and water in liquid paraffin and arachis oil dispersions. Determination of the extinction times of the organism in the systems showed that the bactericidal activity was governed by the concentration of phenol in the aqueous phase and the proportion of oil to water.

The Parabens have been used in combination with other preservatives, for example phenoxyethanol. This combination (marketed as Phenonip) is claimed to have a wide antimicrobial spectrum of activity, the activity being retained in the presence of surfactants and proteins.[38] A synergistic effect has been reported between Phenonip and hexachlorophene, cetylpyridium chloride, thiomersal or dichlorophene.[51] Imidazolidinyl urea has been found to act synergistically with other preservatives including methyl and propyl Parabens, increasing the antimicrobial capacity of the preservative system and the spectrum of antimicrobial activity.[36]

Synergism has also been found to occur with combinations of benzalkonium chloride or chlorhexidine with some aromatic alcohols.[52] Hugbo[53] has reported synergism between *p*-chloro-*m*-cresol and benzalkonium chloride, *m*-cresol and phenylmercuric acetate, and benzalkonium chloride and phenylmercuric acetate.

Partition Coefficient

The preservation of formulations containing oil and water is complicated by the ability of preservatives to distribute themselves between these two phases. Since micro-organisms only grow in the aqueous phase it is important that the preservative does not distribute itself in such a way as to leave an ineffective concentration in this phase. Ideally a preservative should have high water solubility and low oil solubility, that is, have a low oil–water partition coefficient. For simple systems where no emulgent is present the concentration of the preservative in the aqueous phase (C_W) can be calculated from the following equation:

$$C_W = \frac{C(\phi + 1)}{(K_w^o\phi + 1)}$$

where C is the total preservative concentration, ϕ is the oil–water ratio and K_w^o is the oil–water partition coefficient.[54] The concentration of preservative in the aqueous phase is influenced by the oil–water ratio. As a general rule, when $K^o_w < 1$ the aqueous concentration is increased by increasing the proportion of oil, and when $K^o_w > 1$ an increase in the proportion of oil decreases the aqueous concentration.

The partition coefficient itself varies with pH and the nature of the oil. Some oils are predominantly hydrocarbon, whereas others, for example vegetable oils, contain oxygen atoms. Preservatives such as chlorinated phenols form hydrogen bonds with the latter type of oil giving them a high partition coefficient and thus rendering the preservative unsuitable for systems containing this type of oil. However, chlorinated phenols are suitable preservatives for formulations based on oils that are predominantly hydrocarbon.[39] The solubilities of some preservatives in oil and water are given by Cowen and Steiger.[39]

Various workers have shown that the addition of propylene glycol to the water phase of an emulsion reduces the partition coefficient and thus makes more preservative available in the water phase. De Navarre[55] found propylene glycol to be a reliable preservative at 16 per cent in many cosmetic products and stated that its antimicrobial properties were three or four times greater than those of an equivalent amount of glycerin. Propylene glycol does not appear to act solely by virtue of its osmotic effect, showing toxic effects on some micro-organisms at high concentrations.

For systems containing oil and water phases and an emulsifying agent, the preservative concentration in the aqueous phase may be further reduced by binding or solubilization of the preservative by the surfactant. A voluminous literature exists on the inactivation of preservatives by surfactants, particularly the nonionics, and some aspects of inactivation are dealt with in a subsequent section of this chapter.

Susceptibility of Organisms to Preservative

Several nonionic surfactants, notably Tween 80, polyethylene glycol 1000 monocetyl ether and polyethylene glycol 400 laurate, have been found capable of exerting a 'protective' effect on micro-organisms. Judis[56] showed that Tween 80 protected *E. coli* from the lethal effects of *p*-chloro-*m*-xylenol by preventing in part the leakage of the cell contents, as indicated by the release of radio-labelled glutamate which had previously been added to culture media in which the organisms were grown. Similar phenomena have been observed by Wedderburn[57] using cells of different bacteria suspended in nonionic solutions and then washed thoroughly in saline before exposure to media containing 0·1 per cent of esters of *p*-hydroxybenzoate. Tween 80 and various polyethylene glycol esters protected Gram-negative organisms from the inhibitory effects of the preservative.

Interaction between Ingredients and Preservatives

Apart from chemical incompatibility between the ingredients used in products and the preservatives, physical factors—such as solubilization, adsorption or bonding with active sites—can render preservatives inactive in otherwise chemically compatible systems.

Surface-active agents. Certain cationic surfactants have strong antimicrobial properties and when they are used in combination with other antiseptics or preservatives their effect is additive. The antimicrobial effectiveness of cationics varies according to the length of the hydrophobic chain, the most effective compounds having an alkyl chain length of about twelve to fourteen carbon atoms.

Soaps and anionic surfactants exert mild antimicrobial influences at high concentrations but tend to support the growth of Gram-negative bacteria and fungi at low concentrations.

The preservation of emulsions stabilized with either soap or anionic surface-active agents has not, in general, presented many problems, because, when these agents are used as emulsifiers in creams, the concentration of surfactant in the aqueous phase is tolerably high and usually presents an environment that is hostile to the growth of micro-organisms. Nevertheless, these materials decrease the activity of many preservatives to some extent and this is the result of solubilization of the preservatives in the surfactant micelles. Below the critical micelle concentration (CMC) of a soap or anionic detergent solution, preservatives and antiseptics tend to be potentiated in their action, whereas above the CMC activity is diminished. Bean and Berry[58,59] explain the physicochemical phenomena associated with the efficiency of preservatives in aqueous solutions of soaps and anionic detergents.

Nonionic surfactants are now widely used as emulsifiers for creams and also as solubilizers for perfumes in non-emulsified products. The relationship between these materials and preservatives is thus of great importance. Nonionic surface-active agents inactivate preservatives to a far greater extent than soaps and anionic or cationic detergents and, unlike the other surfactants, most nonionics have no growth-inhibiting properties, thus increasing the necessity for adequate preservation of systems that contain them. They have no denaturing effect on bacterial proteins and many can be utilized by bacteria and fungi as sources of energy. For this reason alone the absence of an effective preservative in nonionic-containing products often becomes unpleasantly apparent in a remarkably short time. However, some nonionic surfactants, notably the more hydrophobic octyl and nonyl phenols, have been shown to possess growth-inhibitory properties.[60] Allwood[60] has shown that combinations of polyoxyethylene octyl and nonyl phenols and some antibacterials, for example 2-nitro-2-bromo-propanediol, produced synergism.

There is a large literature on the subject of nonionic–preservative incompatibility. The fundamental theory has been discussed by Kostenbauder[61,62] and has been recently developed by Kazmi and Mitchell[63–65] and others;[66,67] Manowitz,[68] Wedderburn,[69] Russell[40] and Schmolka[70] have also reviewed this subject.

The hydrophile–lipophile balance (HLB) of nonionic surfactants influences their effect on preservative efficiency. The more oil-soluble nonionics, having HLB values of about 3–6, which are often used in water-in-oil emulsions, have a greater inactivating effect on commonly used preservatives than those with higher HLB values.[71]

The mechanism of the interaction between nonionic surfactants and preservatives has attracted a great deal of attention and there is evidence to support the view that the interaction is attributable in part to micellar solubilization of preservatives by nonionic surfactants and also to complex formation. Complexes appear to be formed by hydrogen bonding between the phenolic hydroxyl group in certain preservatives and the basic oxygen in the ether group of the ethylene oxide adducts. This mechanism cannot, however, account entirely for nonionic–preservative interactions since a high degree of hydrogen bonding, and consequently inactivation, would be expected when carboxymethyl cellulose and gum tragacanth are present, but these materials do not inactivate preservatives to anything like the same extent as the high-molecular-weight polyethylene glycol ester, for example.

Coates and Richardson[72] have examined the activity of cetylpyridinium chloride in aqueous solutions of polyethylene glycol and found that, except for very high concentrations, activity is reduced by the presence of the glycol, although not as much as predicted by binding data. Since polyethylene glycol does not form micelles, these workers suggest that the interaction may be due to an attraction between the electron-deficient pyridinium ring of the antibacterial agent and the electron-rich polyether linkages of the glycol.

Preservatives that appear to be much less affected by the presence of nonionic surfactants are formaldehyde, sorbic acid, benzoic acid and dehydroacetic acid.[57]

Nonionic surfactants form micelles in aqueous solutions at very low concentrations and for this reason, when used either as emulsifiers or solubilizers, will always be present at concentrations well above their CMC. In order to be effective, preservatives must be in solution and 'available' in the aqueous phase of a product and the hydrophile–lipophile characteristics of the preservative will influence its relationship with the nonionic. The more lipophilic preservatives appear to be bound to a greater extent than the more water-soluble compounds, and Patel and Kostenbauder[73] have studied the effect of Tween 80 on methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate. The propyl ester was found to have a far greater affinity for Tween 80 than the methyl ester. At 5 per cent Tween 80, 22 per cent of the methyl *p*-hydroxybenzoate existed as free preservative; under equivalent conditions, only 4·5 per cent of the propyl *p*-hydroxybenzoate existed in a free state. The interaction between the nonionic surfactant cetomacrogol and benzoic acid, *p*-hydroxybenzoic acid, methylparabens, propylparabens and chloroxylenol has been investigated and partition and binding phenomena discussed by Kazmi and Mitchell.[65] Konning[66] describes the interaction between phenol or chlorocresol and polysorbate 80 in arachis oil–water systems, and discusses the effect of altering the surfactant concentration and the proportion of oil on the concentration of preservative in the aqueous phase.

Baley *et al.*[67] have investigated the bactericidal properties of some quaternary ammonium compounds in dispersed systems. The concentration of quaternary in the aqueous phase was varied by using different hydrocarbons, different concentrations of hydrocarbons and different surface-active alcohols, and it was demonstrated that the bactericidal activity corresponded to the concentration of free preservative in the aqueous phase.

Attempts have been made to describe the systems mathematically in order that the quantity of preservative required to produce effective preservation in a surfactant solution or emulsified system may be calculated. Kazmi and Mitchell[63] have derived separate equations for surfactant solutions and for emulsified systems which were found to correlate with experimentally determined values. In another paper[64] they developed the theory of capacity. In a solubilized system micelles act as a reservoir of preservative. Any loss of preservative from the aqueous phase—for example due to interaction with micro-organisms, product ingredients or packaging—will lead to an adjustment of preservative concentration in the other phases until the equilibrium is re-established. A method for calculating the capacity of surfactant solutions and emulsions is given. However, since these systems are complex and many variable factors are involved, the concentration of preservative given by mathematical considerations can be regarded only as a starting concentration which must be subjected to microbiological evaluation within the product.

Schmolka[70] has investigated the effects of nonionic surfactants on cationic antimicrobial agents and gives methods by which the interaction can be influenced to produce a satisfactorily preserved product.

Parker[74] has reviewed the methods that have been used to measure the interaction between preservatives and macromolecules used in creams.

Hydrophilic polymers, including high-molecular-weight polyethylene glycols, gum tragacanth, methyl cellulose, carboxymethyl cellulose and polyvinyl pyrrolidone, have only a marginal effect in reducing the efficiency of the majority of preservatives. Quaternary ammonium compounds lose activity in the presence of lanolin and methylcellulose.[36] Figure 36.1 summarizes some of the work showing the degree of binding of methyl *p*-hydroxybenzoate by various macromolecules.

Several workers have reported the successful addition of certain materials to the aqueous phase of emulsions to minimize the inactivating effect of nonionic surfactants on preservatives. Materials such as propylene glycol, glycerin and hexylene glycol change the partition coefficient of the preservative between the phase of the emulsion, thus making more preservative available in the aqueous phase. Ethyl alcohol, propanediol, butanediol and methyl-pentanediol have also been reported as being useful for this purpose.[75]

Influence of Solid Particles on Preservatives. A large number of different insoluble solids are used in cosmetic and toilet preparations. These include talc, kaolin, titanium dioxide, tartaric acid, zinc oxide and chalk, as well as the insoluble solids used to colour creams and the natural and synthetic pigments, all of which present surfaces on to which adsorption of preservative will occur. The extent of this adsorption depends upon the nature of the solid, the type of preservative and the pH of the system. For any particular solid, knowledge of the surface electrical charge under particular conditions in the product, of the total surface area presented to the aqueous phase and of any ion exchange mechanisms which might operate, should enable reasonable predictions to be made about the quantity of preservative lost to the surface.

McCarthy[76] has studied the effects of particulate solids on various commonly used preservatives and has quantified the loss of active material due to adsorption and to factors associated with changes in pH. Clarke and Armstrong[77] showed that kaolin will adsorb benzoic acid and that the extent of the adsorption can be adjusted by regulation of the pH.

Surfactants adsorb on to solid surfaces so that the order of addition of ingredients during manufacture can influence preservative adsorption. If the preservative is dissolved in a slurry carrying the suspended solid particles,

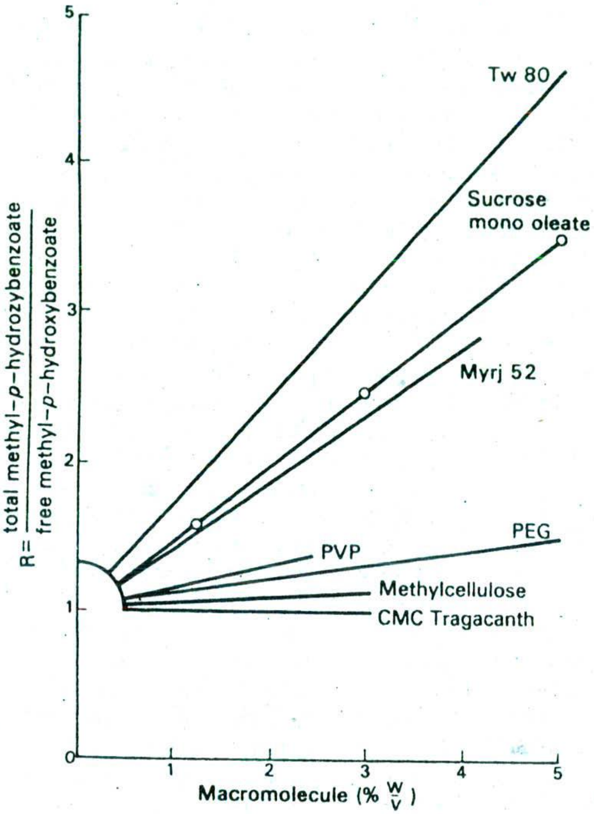

Figure 36.1 Ratio of total to free preservative concentration in the presence of different concentrations of macromolecules (*R* value of 1·0 corresponds to no measurable binding[61])

greater adsorption will occur than if it is added after the particle surfaces have become coated with surfactant.

The activity of a preservative may be reduced by interaction with, or loss through, the container or closure. Interaction of preservatives with rubber has been well documented.[4,40] There is increasing interest in the interactions between preservatives and plastics. Phenolic and quaternary ammonium compounds have been reputed to react with polyurethane.[39] Parabens, benzoic, sorbic and salicylic acids are taken up by nylon, polyvinylchloride and polyethylene.[78]

Selection of a Preservative

Although it is not possible to lay down a set of 'rules' to which a formulator should adhere, weeks of work can often be saved by considering on a theoretical basis the factors that are likely to influence the preservation of a new product.

This approach, coupled with simple laboratory tests on various combinations of the formula components, while not a substitute for thorough microbiological testing of the finished formula, can save time and frustration.

The complexity of modern formulae often means that there is a variety of materials present, some of which will act in favour of good keeping qualities while others will act against whatever preservative is chosen; the relative hostility of micro-organisms or the nutritive value of the formula itself is also of importance.

Obvious steps to follow before selecting a preservative are listed below.

1. Check ingredients for the likelihood of contamination (for example water, materials of natural origin, packaging, etc.).
2. Consider which materials might provide sources of energy for microbial growth (for example glycerin, sorbitol, etc., at concentrations below 5 per cent; nonionic surfactants at almost any useful concentration; soaps and anionic surfactants at concentrations below about 15 per cent, proteins, carbohydrates, cellulose derivations and natural gums).
3. Determine the pH of the aqueous phase of the product before attempting to use any of the preservatives that depend strongly on being in an undissociated form for their activity (see Table 36.6 for percentages of preservatives undissociated related to pH). Consider changing the pH to provide enhanced antimicrobial activity.
4. Depending on the ratios of water and oil present in the formula, estimate whether certain preservatives will be partitioned between the two phases, possibly leaving insufficient in solution in the aqueous phase to be effective. Decide whether any of the materials in solution in the aqueous phase are likely to reduce the partition coefficient (for example propylene glycol and hexylene glycol) and thus tend to help the effectiveness of the preservative or alternatively, increase the partition coefficient (for example surface-active agents), thus reducing its effectiveness. Consider the possibility of adding agents which will alter the partition coefficient or the CMC; for example, urea increases the CMC of nonionic surfactants, thus reducing the number of miscelles and the degree of preservative inactivation.[70]
5. As a guide, estimate the approximate ratio of total to free preservative in the presence of macromolecules in the formulation, and multiply the normally effective concentration by the appropriate factor (see Table 36.7). Formulae derived by Kazmi and Mitchell,[63] as described earlier, may be used to estimate the total concentration of preservative to be added to solubilized systems or emulsions stabilized by nonionic surfactants to give the required concentration of free preservative in the aqueous phase. Equations relating preservative capacity to surfactant concentration and the interaction between surfactant and preservative may also give useful data.[64]
6. Choose the least toxic of the possible preservatives for the system, in order that sufficient quantity can be included to provide a long shelf-life.

Although it is tempting to consider first in any new formula those preservatives that have stood the test of time and are well known, several less obvious choices should be tried in systems which appear difficult to preserve. Some such

Table 36.7 Approximate Ratios of Total to Free Preservative in the Presence of Macromolecules

Preservative	**2% Tween 80**	**5% Tween 80**	**2% Myrj 52**	**5% Myrj 52**	**2% PEG 4000**	**5% PEG 4000**	**2% Methyl cellulose**	**5% Methyl cellulose**
	Factor by which normal concentration of preservatives should be multiplied							
Methyl *p*-hydroxybenzoate	2·5	4·5	2·0	3·0	1·2	1·5	1·05	1·25
Ethyl *p*-hydroxybenzoate	5·0	11·0	3·0	5·0	1·3	1·6	—	—
Propyl *p*-hydroxybenzoate	12·5	27·0	6·0	13·5	1·4	1·7	—	—
Butyl *p*-hydroxybenzoate	30·0	63·0	18·0	40·0	—	—	—	—
Phenol	1·6	2·5	—	—	1·2	1·25	—	—
Sorbic acid	1·8	2·9	1·7	2·7	1·1	1·2	—	—
Cetylpyridinium chloride	38·0	60·0	—	—	—	—	—	—
Benzalkonium chloride	3·0	5·5	—	—	—	—	—	—

materials are:

Bronopol (2-bromo-2-nitro-1,3-propanediol) which, according to Croshaw *et al.*,[79] is active at low concentrations against *Pseudomonas* species, is only slightly reduced in activity by nonionics and has low toxicity.

Chlorhexidine (*bis*(*p*-chlorophenyl-diguanido)hexane), is a wide-spectrum antimicrobial agent with a good record of safety.

Dehydroacetic acid, which is suitable for formulae of low pH, is relatively unaffected by the presence of high levels of nonionic emulsifiers and appears to be safe for use on the skin.

Imidazolidinyl urea, which is not pH-dependent, has high water solubility, is non-toxic, non-irritating and non-sensitizing. It is active against Gram-positive and Gram-negative bacteria, but selectively active against yeasts and moulds. It retains its activity in the presence of many cosmetic ingredients, including surfactants, and frequently acts synergistically with other preservatives, for example Parabens.[36]

Mixtures of preservatives that are effective against different micro-organisms are also often useful. For example β-*p*-phenoxy-ethyl alcohol, which is highly active against Gram-negative bacteria and fungi, can be used with a quaternary ammonium compound such as benzalkonium chloride which acts against Gram-positive bacteria at very high dilutions. In addition there are advantages in using combinations which are not only active against a wide range of organisms but also act synergistically, for example imidazolidinyl urea and Parabens.

Safety Aspects

Preservatives are commonly expensive ingredients and it is always advisable to use the lowest effective concentration. The cost, however, is secondary to the more important question of safety to the consumer.

If tests to measure the effectiveness of certain preservatives show that several times the usual concentration is required to achieve the desired antimicrobial action (because of increased partitioning into the non-aqueous phase, physicochemical binding or factors influencing dissociation), it is wise to consider the toxicity of the preservative at the higher concentration before proceeding. Although a preservative may be partially bound in a product and the remaining fraction in the aqueous phase may represent no more than is safely used in other formulae, the ratio of bound to free preservative is unlikely to remain unchanged when the product is actually in use. Thus from a toxicity point of view the *total* amount is important rather than only that fraction which is acting as a preservative in the particular vehicle. Application of the product to the skin, for example, will disturb the original preservative equilibrium between the various phases of the product and will almost certainly result in liberation of the preservative previously bound. Evaporation of water will increase the concentration of the preservative available to the skin and may result in primary irritation or, in some cases, sensitization.

However, rather than a sharp dividing line between a toxic and a non-toxic concentration of preservative there is, instead, a reasonably continuous spectrum of toxicity, ranging from the very low concentrations to which a few people may show an adverse reaction, to the high levels where both primary irritance and allergic responses will be more numerous. The toxicology of the *p*-hydroxybenzoate esters has been throughly studied and no primary irritation following their use at concentrations up to about 0·3 per cent has been reported. Levels of between 5 and 10 per cent have been used in powders, ointments and solutions to treat athlete's foot and, even at these levels, adverse reactions have not been numerous. Cases of sensitization to the *para*-hydroxybenzoate esters have been reported by Hjorth and Trolle-Lessen[80,81] and also by Sarkany.[82] They showed that it was necessary to use higher concentrations of the preservative than are normally employed in products in order to identify true skin allergies in their standard 48-hour patch test. These results were subsequently confirmed by Schorr[83] in the USA, who found that the allergy usually occurred when chronic contact dermatitis caused by other chemicals was being treated with creams and lotions containing *para*-hydroxybenzoate esters. After an extensive study he concluded that these preservatives are relatively safe in comparison with others commonly used on the basis of their sensitization potential. However, saturated solutions may cause irritation of the eye.[36]

Sorbic and benzoic acid have also been used in products at concentrations far in excess of those required for normal preservation. Benzoic acid appears to have a reasonably clear bill of health but sorbic acid has caused primary irritation characterized by erythema and itching at concentrations below 0·5 per cent.[84]

Sensitization to sorbic acid has been reported by Hjorth and Trolle-Lassen,[80] a well as by Schorr[83] who carried out a large comparative study. In this he found that the incidence of sensitization to sorbic acid was somewhat lower than to the esters of *para*-hydroxybenzoic acid and concluded that if used at concentrations of about 0·2 per cent it was unlikely to constitute a safety hazard.

There is little in the literature to indicate adverse effects brought about by dehydroacetic acid; its widespread use as a food preservative, and the fact that it is relatively little affected by the presence of nonionic emulsifiers, indicate that it merits more consideration as a toilet preparation preservative than it has commanded in the past.

The organic mercury compounds are, of course, recognized poisons. Although they have for a number of years apparently been safely used at concentrations below 0·01 per cent, they present a toxicity hazard to those who have to handle them in concentrated form in factories. Several leading scientists have advised against the use of phenyl-mercuric acetate, borate, and nitrate and also methiolate, on the grounds of their ability to penetrate the skin and endanger the liver and kidneys.

In the USA the Food and Drug Administration has ruled[85] that mercurial preservatives should not be used in cosmetics. An exception is made in the case of eye-area cosmetics because the mercury compounds (up to a limit of 50 ppm) are very effective in preventing *Pseudomonas* contamination; *Pseudomonas* infection of the eye can lead to serious injury or blindness.

The quaternary ammonium compounds have been extensively tested for skin irritation and sensitizing properties. At concentrations below 0·1 per cent most of those commonly used as preservatives appear to cause little or no irritation;

higher concentrations can cause erythema and drying of the skin. Cases of sensitization to cetrimide at concentrations of about 1 per cent have been reported by Cruickshank and Squire.[86] Their substantivity to the human skin has caused concern about plant safety.[87]

Formaldehyde is well known to be a skin irritant, and for this reason, and for reasons of volatility and odour, it has not been used extensively as a preservative. In some countries such as Japan and Sweden its use is banned.[36] Slow formaldehyde-release agents appear to possess less sensitizing potential.[39]

The toxic thresholds of preservatives will depend not only upon the concentrations at which they are used but also upon the vehicle. A certain concentration of a particular preservative may be quite harmless in one system while the same level might evoke adverse skin responses in another because of the presence of substances which increase its penetration through the skin.

Tests for Preservative Effectiveness

Initial Screening Tests

Agar plate tests can be used to obtain a rough indication of whether a particular preservative is likely to be effective but the results should be interpreted with caution.

The test normally involves the use of agar plates seeded with a variety of micro-organisms; wells are cut in the seeded agar and small amounts of the product under test are placed in the wells before incubation of the plates. Gram-negative and Gram-positive bacteria, together with fungi typical of those which frequently contaminate toilet preparations, are listed in Table 36.8 and confirmatory tests for preservation should be carried out using organisms of these or similar kinds.

In this type of test some of the preservative will inevitably diffuse into the agar leaving a lower concentration than was originally present in the product in the well. Although this kind of test can give a rapid indication of whether the preservative shows any likelihood of being effective in the product, it is not by any means definitive and should not be used as a substitute for longer-term and more rigorous evaluation.

Table 36.8 Typical Contaminants of Toilet Preparations

Gram-positive bacteria	Gram-negative bacteria
Staphylococcus aureus	*Pseudomonas aeruginosa*
Streptococcus mitis	*Escherichia coli*
Bacillus subtilis	*Enterobacter aerogenes*
Fungi	**Yeasts**
Aspergillus niger	*Monilia albicans*
Penicillium chrysogenum	*Candida*
Alternaria solani	

Because all the factors governing preservative effectiveness are not at present completely understood, it is almost impossible to predict with certainty whether a particular preservative in a particular system will be efficient. Consequently during the fairly early stages of formulation some microbiological testing must be undertaken to check the compatibility of the preservative in the new system.

Inoculation Tests

Methods by which known numbers of bacteria or fungi are introduced into the product and samples taken at intervals to estimate survival are by far the most reliable. Various test procedures have been proposed[6,88,89] and have been reviewed by Cowen and Steiger.[90] In general, ascertaining the resistance of a product to bacterial contamination involves inoculating a suitable size sample (for example 10 g) of the product with the test organism to give a final concentration of $10^5 - 10^7$ organisms g^{-1}. The number of survivors in the sample is determined at intervals after storage at room temperature. The standard which must be met in order that a product may be considered effectively preserved varies depending on its intended use. Differences in opinion regarding interpretation of results are reflected by the different standards set by the USP test, the Society of Cosmetic Chemists test and the Toilet Goods Association test.

Longer-terms tests, in which smaller numbers of micro-organisms are used and the samples are observed for changes in their physical characteristics over several months, may be more meaningful. Products inoculated with spore-bearing organisms can only be observed for physical changes, as microbiological sampling is unrealistic since spores which might remain dormant in the product will germinate when transferred to nutrient culture medium. In samples inoculated with vegetative organisms, a gradual diminution in numbers can be traced over a period of time if the preservative is effective, but with fungi and spore-bearing organisms one can only wait for the appearance of visible spoilage and this sometimes takes several months to occur.

Inoculation tests have been known to produce misleading results when organisms, artificially introduced into a product, have died off in a short time and the product has been considered to be adequately preserved. Then, later, perhaps during manufacture at the factory or on storage, the product has shown the effects of contamination. One reason for this is that the wrong types of organism were used for the test, and time and the right conditions were not provided for adaptation of the organisms to their environment. Test organisms should be chosen to represent the types of organism that are known to be frequent product contaminants, for example *Pseudomonas* species, and those with which the product is likely to come into contact, for example *Staphylococcus* species. In addition, organisms isolated from the manufacturing environment, raw materials and, where possible, from contaminated products (preferably of the same or similar formula) should be used. In the testing of shampoos, for example, tap water provides a suitable source of test organisms.[8]

The maintenance of test organisms is crucial since their resistance is influenced markedly by the medium on which they are grown. To ensure suitable resistance, test organisms may be grown in a medium containing the preservative or product in low concentration.[91] Product contaminants may be kept in unpreserved or inadequately preserved preparations.[88,92]

Mixed cultures may be used initially to reduce the amount of testing required to assess the adequacy of the preservative system, while pure culture challenge may be employed to give more detailed information about preservative adequacy against specific organisms.[93]

Most tests run for a minimum of 28 days, the product being sampled for viable organisms at various intervals, depending on the probable frequency of usage during this period. Slow adaptation of micro-organisms to their environment makes it essential to test for long enough to determine whether inoculated bacteria and fungi will grow after a dormant period, and in some instances tests lasting as long as six months may be too short.

Tests should also be performed on products that have been stored for specified time intervals at temperatures and humidities which the product is likely to meet during use, in order to ensure that adequate preservative activity is retained throughout the shelf-life.[92] A concurrent chemical assay of the preservative gives additional valuable information.

Products may be tested using a single inoculation or using an inoculation–sampling cycle.[8] The latter method, in which the sample is subjected to more than one challenge, has been advocated by several workers[90] since it is considered to be more representative of in-use conditions and has the advantage of indicating at what point the preservative system will fail. A criticism of the capacity test is that it may lead to excessive preservation, with consequential use of dermatologically unsafe preservative concentrations. The balance between over-preserving and under-preserving a product will depend on the number of challenges, which can only be chosen after a period of experimentation.[90]

In all cases the challenge should take place with the product in the container in which it will be used by the consumer.[92]

Current UK Regulations Relating to Microbial Quality Control of Cosmetics and Use of Preservatives

Microbial limits and guidelines for cosmetic products have been issued by several national trade associations including the Cosmetic, Toiletry and Perfumery Association (CTPA) in the UK. In 1967 the Society of Cosmetic Chemists of Great Britain appointed a working party to draw up a Code of Practice for the cosmetics industry.[6] This Code of Practice, which was published in 1970, covers many aspects of quality assurance including design and operation of manufacturing processes to minimize contamination, microbiological testing procedures and factors influencing choice of preservatives. The working party also initiated several surveys of microbiological quality of UK products; based on this information, the CTPA published in 1975 a set of recommended microbiological limits and guidelines.[94] These indicate that cosmetics and toiletries should comply with the following limits:

Aerobic bacteria	Less than 1000 colony-forming units per g or ml.

Yeasts and moulds	Less than 100 colony-forming units per g or ml.
Products intended for use in the eye area and for use on babies	Less than 100 colony-forming units per g or ml.
Harmful organisms	Wherever significant numbers of colonies are observed, the presence of harmful organisms should be excluded.

Preservatives
A proposed amendment to the EEC cosmetics directive[95] contains a list of preservatives for use in cosmetics and toiletries. This list is divided into two parts. The first part includes eleven preservatives that are considered acceptable for use in cosmetics, while the second part is a 'provisional list' of 56 preservatives which may be considered acceptable subject to provision of further information regarding their safety over the period up to 1982. At the time of writing the amendment has not been incorporated into the directive.

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Chapter Thirty-seven

Antioxidants

Introduction

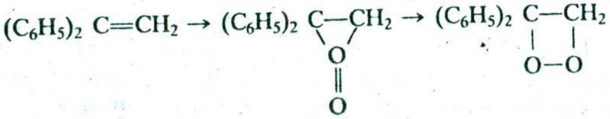
The ability of atmospheric oxygen to act as an oxidizing agent for fats, fatty acids and many other organic materials is of commercial importance. In some cases the phenomenon may be advantageously employed, but in cosmetics the effects of oxidation are normally deleterious and can lead to complete spoilage. Although the literature on the chemical and physical changes involved in oxidation is extensive and can be traced back to the eighteenth century[1] it is only in the past thirty-five years that the mechanisms involved have been understood with any degree of certainty.

Two of the problems associated with an understanding of the general oxidation reactions have been the very wide spectrum of organic materials which are subject to this type of decomposition and, secondly, the large number of factors which can effect both the rate and course of the reactions. Amongst these latter may be numbered the effects of humidity, oxygen concentration, temperature, UV irradiation and the presence or absence of anti- and pro-oxidants. In the early studies of oxidative reactions many of the above environmental conditions were not recognized as being important and were therefore not controlled, so that the results obtained are in many cases invalidated. Another problem with the generalized oxidation theories which were developed from this early work was that it was found difficult to apply the results from simple reference substances such as methyl oleate or methyl linoleate to more complex naturally occurring materials such as sunflower seed oil or soya bean oil, particularly at the high temperatures sometimes reached during the purification or processing of these products. Other difficulties were encountered when the general oxidation scheme was applied to organic materials other than fats and their derivatives.

General Autoxidative Theory

The bulk of development work on a generalized theory of autoxidation was concerned with the reactions of olefinic materials and consequently the study of the reactivity of the carbon–carbon double bond is of paramount importance. This reaction was first studied by Schönbein[2] using almond oil; it was not until almost half a century later, when the effect of organic peroxides on oxidation was studied by Engler and his co-workers,[3,4] that the modern oxidative theory began to be formulated. Engler believed that the reaction was due to molecular rather than atomic oxygen producing a substance $R_1—O—O—R_2$ which in turn could oxidize other oxidizable substances when the loosely held 'molecular activated' oxygen was released. This led Fahrion[5] to assume the formation of a cyclic peroxide which could at later stages of the oxidative reaction rearrange to form dihydroxyethylenic or hydroxyketo compounds along with more stable ethers. Until the development of the modern chain reaction theory of oxidation this ring peroxide theory was generally accepted by most workers in the field. However, the mechanism was never fully developed and increasingly it became apparent that the autoxidation mechanism was more complicated.

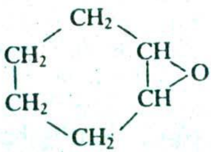
At a fairly early date Staudinger[6] had suggested, from studies using *asym*-diphenylethylene, $(C_6H_5)_2C{=}CH_2$, that ring peroxide formation was the second stage of the reaction and that primary oxidation involved the addition of a molecule of oxygen across the ethylene bond to form a moloxide which subsequently rearranged to the cyclic peroxide:



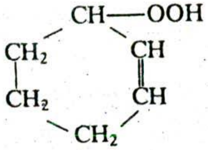
The problem with the cyclic peroxide oxidation theory was that only indirect evidence for the existence of such compounds could be obtained. Most of the evidence for their existence came from determinations of carbonyl, diene, hydroxyl, iodine, peroxide and saponification values. These were considered alongside determinations of molecular weight and the total oxygen uptake. The problem was that the analytical results obtained were unreliable because the oxidizing material was usually a non-fractionated natural product which would, of necessity, show batch-to-batch variations in the proportion of individual components and, as a consequence, exhibit variable oxidative behaviour. It was also not realized that many of the analytical techniques used were not strictly quantitative.

Alongside the ring peroxide theory existed the suggestion due to Fokin[7] that the initial stage in the oxidation was the formation at the ethylene bond of an epoxide of the type which can be isolated from many oxidizing peracids and other oxidizing mixtures, but it is doubtful if these represent primary products in the normal oxidation reaction.

The development of the modern theory of autoxidation may be said to start from the isolation of a cyclohexene peroxide by Stephens in 1928.[8] On the basis of theories then current he assumed that this was a saturated product with a possible formula:

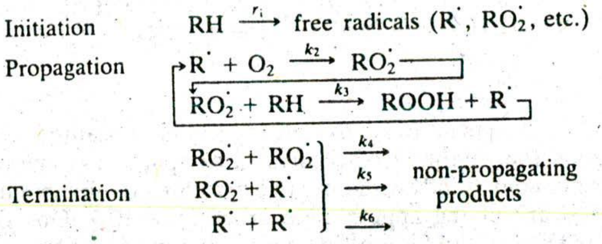


However, Farmer and Sundralingam[9] showed that this interpretation was incorrect and that Stephens' compound was an unsaturated hydroperoxide:



Farmer and his co-workers[10–15] developed these observations into the now generally accepted theory of autoxidation by means of a free radical mechanism involving the formation of hydroperoxides. According to this theory the reaction involved the addition of one molecule of oxygen at a carbon atom α- to the double bond; while more recent work has suggested that this is probably not the primary reaction, it would appear that it is the reaction responsible for the propagation of the chain mechanism. Hargrave and Morris[16] have suggested that an alternative path for reaction between a peroxy radical and an olefine molecule may exist and that oxygen would be partitioned between hydroperoxide and diperoxide groupings. Breakdown of the olefin during oxidation is thought to lead also to the formation of carbonyl and carbinol compounds.

From these studies of individual oxidizable compounds, a general kinetic scheme for autoxidation was developed[17,18] and may be represented as:



where RH is an olefine and $RO_2^{\cdot}$ and $R^{\cdot}$ are hydroperoxide and olefinic free radicals.

This scheme shows a typical free radical reaction mechanism where free radicals of outside origin may catalyse or inhibit the reaction and where the rate may be shown to be dependent upon the square root of light intensity.

It can be shown that the reaction $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ is extremely rapid, which means that at most normal oxygen pressures, the termination reactions $R^{\cdot} + R^{\cdot} \rightarrow$ and $R^{\cdot} + RO_2^{\cdot} \rightarrow$ may be ignored as the concentration of $RO_2^{\cdot}$ will greatly exceed $R^{\cdot}$.

The determined experimental rate equations for olefinic oxidation under a number of conditions showed that a common equation was applicable:

$$\text{Rate} = R_1^{1/2}k[\text{RH}]\cdot\frac{[\text{O}_2]}{k'[\text{RH}] + [\text{O}_2]}$$

where R_1 is the rate of formation of chain carriers and k, k' are constants. It has been shown that because $(k_4 k_6 R_1)^{1/2}$ is negligible in long-chain-length reactions there would be complete correlation between the experimental and theoretical equations:

$$\frac{-\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = R_1^{1/2} \cdot \frac{k_3}{(k_4)^{1/2}} \cdot [\mathrm{RH}] \frac{k_2(k_4)^{1/2}[\mathrm{O_2}]}{k_3(k_6)^{1/2}[\mathrm{RH}] + k_2(k_4)^{1/2}[\mathrm{O_2}] + (k_4k_6R_1)^{1/2}}$$

Uri[19] has applied stationary state conditions and produced the following kinetic equations:

$$\begin{aligned}
&\mathrm{d}[\mathrm{R}^{\cdot}]/\mathrm{d}t = r_1 - k_2[\mathrm{R}^{\cdot}][\mathrm{O_2}] + k_3[\mathrm{RO_2^{\cdot}}][\mathrm{RH}]\\
&\mathrm{d}[\mathrm{RO_2^{\cdot}}]/\mathrm{d}t = k_2[\mathrm{R}^{\cdot}][\mathrm{O_2}] - k_3[\mathrm{RO_2^{\cdot}}][\mathrm{RH}] - k_4[\mathrm{RO_2^{\cdot}}]^2\\
&\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = (r_1/k_4)^{1/2} \times (k_3[\mathrm{RH}])
\end{aligned}$$

At low oxygen level termination reactions involving $\mathrm{R}^{\cdot}$ become significant and these kinetics would have to be modified to take account of this fact. Uri therefore proposes a more general rate equation equivalent to that of Bolland[17] and Bateman[18] for the formation of peroxide:

$$\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = (r_1/k_4)^{1/2} \cdot k_3[\mathrm{RH}] \frac{k_2(k_4)^{1/2}[\mathrm{O_2}]}{k_3(k_6)^{1/2}[\mathrm{RH}] + k_2(k_4)^{1/2}[\mathrm{O_2}]}$$

He further suggests that provided $k_6 = k_4$ this may be simplified to:

$$\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = (r_1/k_4)^{1/2} \cdot k_3[\mathrm{RH}] \frac{k_2[\mathrm{O_2}]}{k_3[\mathrm{RH}] + k_2[\mathrm{O_2}]}$$

Oxidation of Mono-unsaturated Systems

Because of the slow speed of autoxidation in mono-unsaturated systems, it is normal to study the catalysed reaction. If a comparison is made between the oxidation rate of compounds with one, two and three double bonds respectively then the ratios are of the approximate order 1:12:20.[19] One of the earliest studies was by Farmer and Sutton[12] who managed to extract a pure hydroperoxide from oxidizing methyl oleate using a technique of molecular distillation and chromatography. This work was extended by other workers[20,21] to obtain hydroperoxide concentrates from oxidizing methyl oleate. Originally Farmer suggested that a variable mixture of mono- and dihydroperoxides was formed at the eighth or eleventh carbon atom of the oleate chain. Privett and Nickell[22] showed that the α-hydroperoxides predicted by the general theory are formed in approximately equal proportions. It is not certain that only hydroperoxides are formed from mono-unsaturated compound oxidation, as polarographic analysis[23] indicates a significant wave in a region not normally associated with hydroperoxides. It has been suggested that this wave corresponds to cyclic hydroperoxides.

The problem with the hydroperoxide chain mechanism for mono olefine oxidation is that a large amount of energy is required to break an α-methylenic C–H bond and Farmer[14] and other workers[24,25] suggested that there must be a small primary attack at the double bond and that the products of this attack initiated the normal α-methylenic chain reaction.

Because of resonance around the double bond the hydroperoxide can be shown to produce a double bond shift[15] in the oxidizing mono olefine.

Oxidation of Nonconjugated Polyunsaturated Systems

The rate of oxidation of nonconjugated polyunsaturated systems is very much more rapid than that of those containing only a single double bond. This is due to the activation brought about by the presence of a methylene group adjacent to two double bonds. The presence of this type of compound in the fats and oils used in cosmetics is the main source of oxidative rancidity.

While Farmer[26] had observed that in the early stages of oxidation the oxygen was used to form peroxide and that the double bonds remained unchanged, it was also soon found that the originally nonconjugated double bonds were now showing a conjugated formation[12] which was not due to the peroxide structure. The degree of conjugation found (70 per cent) was taken as evidence of random attack on the resonating free radicals from the linoleate nucleus; however, Bergström[27] found it impossible to isolate the 11-hydroxystearate from linoleate oxidation, although the hydrogenated oxidation product did allow the isolation of the 9- and 13-hydroxystearates. One of the major problems was that the UV evidence was based on comparison with *trans*, *trans*-10,12-octadecadienoic acid with an extinction coefficient of 32 000. However, it can be shown that *cis*, *trans* isomerism can occur and also that the peroxide group and its position can effect the extinction coefficient. These problems suggested that the value of 70 per cent conjugation might be incorrect. Privett[28] and co-workers suggest that up to 90 per cent of the hydroperoxide is conjugated and consists of the *cis*, *trans* isomers. However, the effect of temperature must also be considered, as at 24°C the *cis*, *trans* isomer appears to rearrange and result in the production of a more stable *trans*, *trans* form. This led Holman[29] to suggest an oxidation mechanism which accounted for these observations (see Figure 37.1).

The oxidation of these compounds is therefore by the normal general hydroperoxide chain reaction developed by Farmer, but it can be shown that an initiating free radical is required as highly purified linoleates and similar compounds exhibit a very long induction period.[30]

With linoleate radicals which contain three nonconjugated double bonds there is a more complicated resonance and in the later stages of oxidation diperoxides could be formed. However, at low temperatures approximately 60 per cent of monomeric *cis*, *trans* conjugated diene monohydroperoxides appear to be formed.[31]

Oxidation of Conjugated Polyunsaturated Systems

Although not studied to the same extent as in the previous systems, the oxidation of conjugated polyunsaturated systems is important and the available evidence suggests that this oxidative mechanism may differ in a number of respects. The oxidative products appear to be noncyclic polymeric peroxides produced by the addition of oxygen to the diene system.[32,33] The attack of oxygen on these compounds produces both 1,2- and 1,4- addition apparently alongside a proportion of α-hydroperoxides. However, fairly simple isomeric differences in the material studied appear to produce profound changes in the products of oxidation.

Thus Allen and his co-workers,[34] studying the oxidation of 9,12- and 10,12-methyl linoleate, found that whereas in the early stages of the reaction of the former compound all the oxygen was in the form of peroxide, in the oxidation of

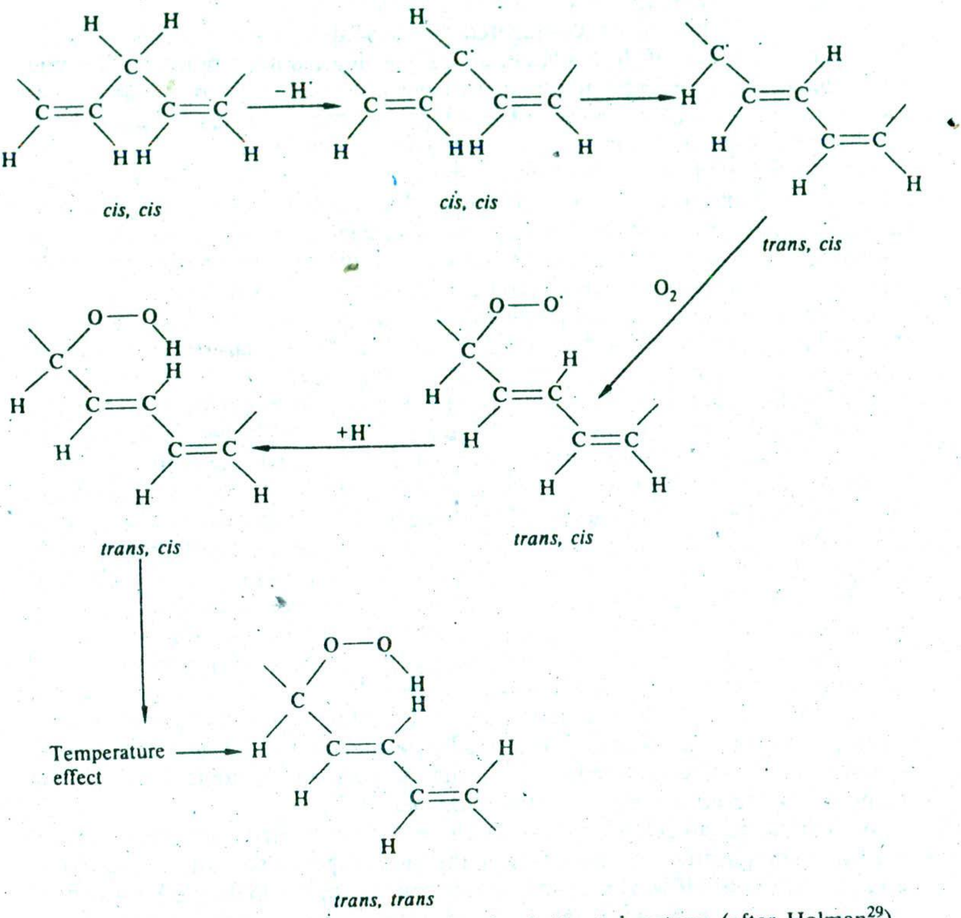
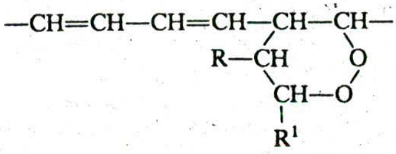


Figure 37.1 Oxidation of nonconjugated polyunsaturated systems (after Holman[29])

the latter compound no peroxide occurred in the early stages. The reaction was accompanied by the disappearance of double bond conjugation which was directly related to the amount of oxygen absorbed, suggesting some form of carbon-to-oxygen polymerization. Metal catalysts have also been shown to have much smaller effects on the oxidation of conjugated systems, suggesting that the decomposition of peroxides did not play a significant role in their oxidation.[35] The relative rate of oxidation of the corresponding conjugated and nonconjugated systems is open to doubt and reports have appeared suggesting both different and similar rates of oxidation, depending upon experimental conditions.[34,36,37] The formation of polymer appears to cause steric hindrance, thus reducing further oxidation, although the corresponding increase in viscosity does not, as such, prevent oxidation even though it slows down the rate of diffusion of oxygen into the system. The products of oxidation from these systems are much more variable. Eleostearate oxidation appears to produce a cyclic peroxide with formula:



although further oxidation is possible.[38] The overall kinetics of oxidation appear to simplify to:

$$dO_2/dt = k[\text{Product}]^{1/2} . [\text{Ester}]$$

These kinetics suggest that propagation is by polymerization, but other studies have suggested an autocatalytic mechanism[36,39] while O'Neill,[40] studying the UV light oxidation of methyl eleostearate, found a complex mixture of products suggesting that both polymeric and autocatalytic processes were taking place simultaneously.

Oxidation of Saturated Systems

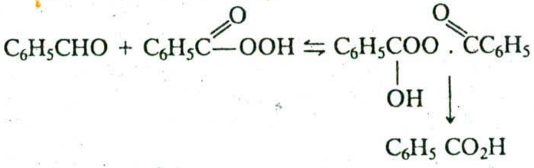
Under the normal conditions of oxidation 'experiments' most saturated compounds appear to be inert, but many unsaturated materials undergo a slow oxidative process at elevated temperatures. If the oxidation rates of the compounds methyl stearate : methyl oleate : methyl linoleate : methyl linolenate are compared at 100°C then the reaction ratio is 1 : 11 : 114 : 179.[19]

The rate of oxidation of saturated hydrocarbon compounds increases with chain length and, while the primary product is a hydroperoxide, the position of attack by the oxygen appears to be random.[41,42] As secondary products, alcohols and ketones, which can themselves undergo further oxidation, are formed at an early stage.

The oxidative behaviour of a number of saturated fatty acids and their derivatives has been studied, at elevated temperatures, by Paquot and de Goursac[43] and it was shown that under their experimental conditions approximately 50 per cent of the material oxidized. β- attack occurred to produce oxalic acid and shorter-chain-length fatty acids. Minor amounts of lactones and methyl ketones were also detected.

Autoxidation of Aldehydes

Aromatic aldehydes, and in particular benzaldehyde, appear to have been the most popular material for study. Almquist and Branch[44] showed that initially a peroxide was formed, the quantity of which subsequently decreased owing to the catalytic effect of the build-up of benzoic acid. This catalytic effect speeded up the reaction of benzaldehyde and the initially formed perbenzoic acid. These two compounds form an adduct whose rate of decomposition into benzoic acid determines the order of reaction:



$$C_6H_5CHO + C_6H_5\overset{O}{C}\text{—}OOH \rightleftharpoons C_6H_5\underset{OH}{C}OO \,.\, \overset{O}{C}C_6H_5 \rightarrow C_6H_5\,CO_2H$$

The possibility that the perbenzoic acid was formed by a chain reaction which could be influenced by light was discussed by Bäckström[45] while later it was shown that heavy metal catalysis could also occur.[46] Waters and Whickham-Jones[47] found that the rate of oxidation was proportional to the square of the benzaldehyde concentration and to the square root of dibenzoyl peroxide concentration, and independent of oxygen concentration.

That other organic aldehydes oxidize through a similar free radical mechanism has been shown by Cooper and Melville[48] using decanal. They showed that the oxygen molecule reacted directly with the aldehyde and that with photoelectric initiation the light was directly responsible for the formation of free radicals.

Oxidation of Ketones

The oxidation of ketones has been less studied than that of aldehydes and appears to require a high temperature to produce decomposition. A temperature above 100°C was found by Sharp[49] to be required and the initially produced hydroperoxide rapidly decomposed to give a mixture of acids and aldehydes.

Antioxidants

General Mechanism

If the general chain propagation reactions for oxidation are valid then it is conceivable that the suppression of oxidation could occur either by suppressing the formation of free radicals or by the introduction into the system of material that would react with free radicals as they were formed, and so prevent a build-up of reaction chains. The formation of free radicals cannot be wholly prevented and therefore substances which behave as free radical acceptors—antioxidants—are important.

Bolland and ten Have[50] studied the effect of hydroquinone (AH) on the oxidation of ethyl linoleate (RH). They suggested that this compound reacted with the free radicals to give:

$$\left.\begin{array}{l} R^{\cdot} + AH \xrightarrow{k_7} \\ RO_2^{\cdot} + AH \xrightarrow{k_8} \end{array}\right\}\text{inactive products}$$

This led to the rate equation:

$$r_a = -d[O_2]/dt = r_i k_3[RH]/k_2[AH]$$

where r_a is the rate of oxidation in the presence of the antioxidant and r_i is the rate of initiation of chains, and where the reaction $R^{\cdot} + AH$ is ignored as being of little importance in the antioxidant reactions. However, Davies[51] has assumed that the free radicals initially formed are $R^{\cdot}$ and thus the rate equation in the presence of antioxidants would become:

$$r_a = -d[O_2]/dt = r_i(1 + k_3[RH]/k_2[AH])$$

The possibility that this equation is significant, at least in the early stages of oxidation, has been cast in doubt by Bolland and ten Have who showed that, when the reaction involved $RO_2^{\cdot}$ radicals, the value $(r_a/r_u^2)[AH][RH]$ was a constant with a value depending on the reaction coefficients $k_4/k_3.k_2$; r_u is the rate of oxygen uptake in the absence of antioxidant. A similar treatment for reactions involving $R^{\cdot}$ radicals did not produce a constant. These authors[50,52] were able to show that with hydroquinone (now designated AH_2) the reaction occurred in two stages involving the intermediate formation of a semiquinone radical. Thus:

$$\begin{array}{l} RO_2^{\cdot} + AH_2 \xrightarrow{k_9} ROOH + AH^{\cdot} \\ AH^{\cdot} + AH^{\cdot} \xrightarrow{k_{10}} A + AH_2 \end{array}$$

The rate constant (k_9) has been shown to be approximately the same for different $RO_2^{\cdot}$ radicals and is therefore of possible importance in the determination of antioxidant efficiency.[48] Except in the initial induction period and the final stages of oxidation it was found that a plot of $1/r_a$ versus time was a straight line and that the rate of initiation was composed of elements due to temperature and light intensity, so that:

$$r_i = k_i[RCHO][O_2] + I$$

where I was the light intensity.

A mechanism involving the intermediate formation of a complex between the free radical $RO_2^{\cdot}$ and the antioxidant has been proposed by Boozer and his co-workers.[53] This would be followed by a subsequent rate-controlling reaction with further $RO_2^{\cdot}$ radicals:

$$RO_2^{\cdot} + AH \xrightarrow{\text{rapid}} [RO_2 + AH]^{\cdot} \xrightarrow[\text{rate controlling } (k_{in})]{RO_2^{\cdot}} \text{products}$$

The rate equation from this reaction would become:

$$r_a = -d[O_2]/dt = \{k_3[RH]/(r_i/k_{in}[AH])\}^{1/2}$$

These kinetics were shown to account for the kinetics of oxidation of tetralin in chlorobenzene with phenol and N-methylaniline as inhibitors and azoisobutyronitrile as initiator. However, Boozer's mechanism appears to occur only with weak antioxidants where the removal of hydrogen by the $RO_2^{\cdot}$ radical from the antioxidant AH is too slow in comparison with its removal of hydrogen from the oxidizing species RH.

Comparison of Antioxidant Efficiency

The comparison of many practical antioxidants was reviewed by Olcott,[54] Banks,[55] Lovern[56] and Lea.[57] Most of the early data were based on the extension of the induction period rather than on the kinetics of inhibition.

Rosenwald[58] has shown that the antioxidant effect per unit of concentration appears to depend on the concentration of antioxidant. An equation:

$$\log \text{induction period} = r + s \log[AH]$$

(where r and s are constants which may have either a positive or negative value) was found. Uri[59] has pointed out the danger of extrapolating comparative results obtained at elevated temperature to lower temperatures or of extrapolating results in an homogeneous phase to two-component emulsified systems.

Many chemical factors have been investigated in the comparison of antioxidant efficiency. Although it can be shown that there appears to be a correlation between oxidation-reduction potential and the antioxidant efficiency of phenols it is possible that this is fortuitous. The activation energy is a better criterion for chemical reactions, and before oxidation-reduction potential can be used it is important to show that it runs parallel with the activation energy changes. Another problem is that while some phenolic systems show well defined but reversible end products, for example quinone from hydroquinone, others have irreversible or partially irreversible end products.[60]

Bolland and ten Have[52] related antioxidant efficiency, as measured by the rate constant for the reaction $RO_2^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$, to the oxidation-reduction potential and by plotting log(relative efficiency) against oxidation-reduction potential obtained an approximate straight-line relationship. They suggest that efficiency increases in proportion to a decrease in the bond dissociation energy A–H and that a limit will eventually be reached when $AH + O_2 \rightarrow HO_2^{\cdot} + A^{\cdot}$ becomes a significant reaction. This view has been challenged by Uri[59] who considers that the reaction $A^{\cdot} + O_2 \rightarrow AO_2^{\cdot}$ is far more critical.

The chemical structure, in particular the form and position of substituents, is also important when considering relative antioxidant efficiency.[51] The basic observation is that electron-repelling groups will increase antioxidant efficiency while the inclusion of electron-attracting groups in an antioxidant will decrease its efficiency. The effect of poly-substitution appears to be additive, but steric factors may interfere with direct comparison, particularly when substitution is in the *ortho* position. It must also be remembered that the addition of oxygen to a simple phenolic —O—H bond would lead to an impossible $—O—O—O^{\cdot}$ structure.

Special problems also exist in the choice and relative efficiency of antioxidants in emulsified and solubilized preparations. With emulsions it is an advantage for the antioxidant to be present at the interface between the oil drop and the continuous aqueous phase. Therefore the antioxidant should exhibit a suitable balance between lyophilic and lyophobic groupings. If it exists in both phases, then in the aqueous phase it will decompose to give free radicals which may initiate oxidation of oil.

Synergism

Synergism is said to occur when two or more antioxidants present in a system show a greater overall effect than can be accounted for by a simple addition of their individual effectiveness. Although this phenomenon is well known, most of the systems have been studied on an empirical basis. The phenomenon is associated with two separate systems: (a) mixed free radical acceptors, and (b) the metal chelating agents.

Mixed Free Radical Acceptors. It would appear that the effect of mixed free radical acceptors is due to both steric factors and activation energy changes.

In a synergistic system involving a material such as ascorbic acid (BH) which has a low steric factor and hydroquinone (AH) in which steric factors would not be important, Uri[59] has suggested that the following reactions will take place:

$$\mathrm{RO_2^{\cdot} + AH \longrightarrow RO_2H + A^{\cdot}}$$
$$\mathrm{A^{\cdot} + BH \longrightarrow B^{\cdot} + AH}$$

The possible disappearance of $\mathrm{A^{\cdot}}$ by reaction with oxygen is thus eliminated and the effective antioxidant AH is regenerated. On its own BH would not produce any significant antioxidant effect as the reaction:

$$\mathrm{RO_2^{\cdot} + BH \longrightarrow RO_2H + B^{\cdot}}$$

would be prevented by steric factors.

Metal Chelating Agents. The normal effect of metal chelating agents is to bond with pro-oxidant metallic ions and thus prevent their catalytic effect on the normal oxidation chain reaction. This reaction does not therefore prevent normal oxidation taking place, but only slows down the formation of peroxide while at the same time extending the induction period. Metallic pro-oxidants that are already present as part of complex organic structures are not usually affected by chelating agents. Stabilization has been achieved by reaction of the metal with organic acids of the tartaric or citric acid type or with materials such as ethylenediaminetetra-acetic acid (EDTA).

Recent reviews of antioxidant–synergist systems have been published by Prosperio[61] and Lozonczi.[62]

Typical antioxidants and synergistic systems used in cosmetics are given in Table 37.1.

Measurement of Oxidation and the Assessment of Antioxidant Efficiency

Tests to measure oxidation and to assess antioxidant efficiency may be similar and in general are designed to measure either the rate of oxidation (by direct measurement of oxygen uptake or the formation of decomposition products) or the extension of the induction period. Many of the tests used are artificially accelerated by the use of UV irradiation or elevated temperature and the extrapolation of such results to normal shelf storage conditions is suspect owing to possible changes in the oxidation reactions under the accelerating conditions. A secondary problem is that many antioxidant combinations are tested on the pure oil or fat and no account is taken of other materials present in the formulation which may materially alter the overall efficiency of the system. Whatever indications accelerated tests give, it is imperative that long-term storage tests are used to confirm the choice of preservative.

One difficulty is that common techniques such as the determination of hydroxyl or iodine values are frequently misleading owing to the interference of other products of the oxidation system, particularly peroxides, and methods of assessing antioxidant efficiency based on such values may give completely false impressions of efficiency. Even the normal estimations of peroxide values must be viewed with a degree of suspicion as they are not very specific and the reactions involved may be non-stoichiometric. However, this is the most common method of measuring oxidation and antioxidant efficiency, although the peroxide measured is the undecomposed peroxide and really indicates that

Table 37.1 Antioxidants for Use in Cosmetic Systems

Aqueous systems

Sodium sulphite
Sodium metabisulphite
Sodium bisulphite
Sodium thiosulphate
Sodium formaldehyde sulphoxylate
Acetone sodium metabisulphite
Ascorbic acid
Isoascorbic acid
Thioglycerol
Thiosorbitol
Thioglycollic acid
Cysteine hydrochloride

Non-aqueous systems

Ascorbyl palmitate
Hydroquinone
Propyl gallate
Nordihydroguaiaretic acid
Butylated hydroxytoluene
Butylated hydroxyanisole
α-Tocopherol
Phenyl α-naphthylamine
Lecithin

Synergistic systems

Antioxidant	*per cent*	*Synergists*
Propyl gallate	0·005–0·15	Citric and phosphoric acid
α-Tocopherols	0·01–0·1	Citric and phosphoric acid
Nordihydroguaiaretic acid (NDGA)	0·001–0·01	Ascorbic, phosphoric, citric acids (25·50% NDGA content) and BHA
Hydroquinone	0·05–0·1	Lecithin, citric acid and phosphoric acid, BHA, BHT
Butylated hydroxyanisole (BHA)	0·005–0·01	Citric and phosphoric acids, lecithin, BHT, NDGA
Butylated hydroxytoluene (BHT)	0·01	Citric and phosphoric acids up to double the weight of BHT and BHA

peroxides are being formed faster than they are broken down. This condition does not necessarily apply in the later stages of oxidation which may only show small peroxide values.

Determination of Peroxides

A large number of methods is available for the determination of peroxides, but the results, while reproducible within a given set of experimental conditions, are difficult to compare from worker to worker as differing experimental techniques will give discordant values even on the same substrate. The technique normally involves the liberation of iodine from sodium or potassium iodide in the presence of peroxide. Lea[63] showed that the system should be acidified during this release, while Knight[64] showed that the presence of other functional groups did not interfere and Swift[20] showed that one mole of iodine was liberated by one mole of methyl oleate hydroperoxide. Lea's method[65] of heating with glacial acetic acid and chloroform in the presence of solid potassium iodide and a nitrogen atmosphere is claimed to detect as little as 10^{-6} equivalents of peroxide per g of fat. The reacted mixture when cooled was added to 5 per cent potassium iodide solution and titrated with 0·002 N sodium thiosulphate. A modification which is in common use is due to Wheeler[66] who, while still using a chloroform–glacial acetic acid solvent (50 ml), used 1 ml of saturated potassium iodide solution and 3–10 g of the oil under investigation.

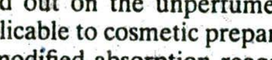
Both of these methods, and many other variations, gave conflicting peroxide values. It has been found that the solvent used and the acid condition will cause variation,[67] and a modified Wheeler technique using sulphuric acid and identical sample weights is claimed to have given the most reproducible values.[68] The importance of constant sample size has been demonstrated by numerous workers as also has the presence of an inert atmosphere to prevent further oxidation during the determination.[69–71]

Other Methods of Analysis

Chemical. Other chemical methods have been employed for the detection of rancidity but all suffer to some degree from the problem of non-reproducibility and difficulty of interpreting the results. However, they are still occasionally used and therefore worthy of mention.

The Kreis test, first described in 1902, is the one most frequently employed to determine oxidative rancidity. In this test 1 ml of the oil (or melted fat) is shaken with 1 ml concentrated hydrochloric acid for one minute; then 1 ml of a 0·1 per cent solution of phloroglucinol in ether is added and shaking is continued for a further minute. A pink or red coloration of the lower acid layer is considered to be indicative of rancidity, the amount of which is approximately (although not exactly) proportional to the intensity of the colour. A preferable modification of this method was suggested by the Committee of the American Oil Chemists' Society, in which the colour is measured by means of glass colour standards in a Lovibond tintometer.

This red coloration is produced by epihydrin aldehyde,



$$CH_2—O—CH—CHO$$

but it should be remembered that a fat is not necessarily rancid if it responds to this test. Fresh, crude vegetable oils may give similar colours, although these usually disappear on refining. Essential oils and aldehydes which may be present in certain toilet articles and cosmetic products can give positive results; hence such tests should be carried out on the unperfumed product.

A modified Kreis test applicable to cosmetic preparations, in which aeration is employed together with a modified absorption reagent, has been described by Jones.[72] This test eliminates the interference of many other substances. Directions are given in the original article for testing various types of cosmetics.

The Schiff test for aldehydes appears to be slightly more sensitive, but the colorimetric evaluation is not so easy with this test and it offers no particular advantage. Since it may be readily found in any textbook, the exact procedure is not described.

Schibsted[73] has developed this test to be specific for aldehydes of a high molecular weight. However, the stipulated conditions must be carefully followed, and for these the original paper should be consulted.

Lea[74] has devised a method by which the relatively minute amounts of aldehydes in a rancid fat may be measured by a simple titration with sodium bisulphite. Some preliminary tests with cotton-seed oil appeared to indicate that this method correlated more closely with the organoleptic test than did the Kreis test.

Another test which has been suggested for the determination of oxidative rancidity is that employing a 0·025 per cent solution of methylene blue in alcohol. About 2 ml of this reagent are added to 20 ml of the oil or fat, which is shaken and the amount of colour reduction taken as a measure of its rancidity.

Lea[75] states that the aerobic ferric thiocyanate method, although it gave high results in the presence of atmospheric oxygen and values too low in its absence, showed excellent reproducibility, required much less material than the iodometric method and under any one set of conditions gave results which appeared to be directly proportional to the iodometric values.

The most commonly used accelerated test is that known as the aeration test, active oxygen method or Swift stability test.[76] The sample is kept at 97·8°C and is aerated with a standard flow of air. From time to time samples are taken and the degree of rancidity is assessed, either organoleptically or chemically, until a predetermined value is reached. The peroxide value is generally chosen as the chemical criterion. Modifications of this involve other temperatures, for example 100°C, at which temperature the time required to attain a given degree of rancidity is about 40 per cent of that in the Swift test. Becker, Gander and Hermann[77] describe a type of Swift test, and Lea[78] describes an accelerated autoxidation test in which fat and water are kept in the closest possible contact.

Chromatography. The presence and concentration of butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and alkyl gallates may be determined by thin layer chromatography which permits the identification of 2 μg of BHA, 4 μg of BHT and 1 μg of alkyl gallate with diazotized *p*-nitroaniline.[79] A chromatographic method has also been used by Dooms-Goosens[80] for the identification of antioxidants. He separated his material by the addition of anhydrous sodium sulphate followed by solubilization with petroleum ether and finally extraction with acetonitrile. A silica gel plate was used in conjunction with a petroleum ether–benzene–acetic acid developing solution.

Determination of Oxygen Uptake. The direct determination of oxygen uptake may be made using the Warburg constant volume respirometer or the Barcroft differential manometer. Detailed methods for the use of these instruments are given by Umbreit, Burris and Stauffer.[81] In essence the method involves the measurement of oxygen taken up in the presence and in the absence of antioxidant and allows both the rate of oxidation and the length of the induction period to be measured. The end of this latter function may be difficult to determine and the time for an arbitrary uptake of oxygen is often used to signify the end of the induction period. Spetsig[82] and Lew and Tappel[83] have both described the use of the Warburg apparatus for the measurement of oxidation rate in a stable emulsion, while Carless and Nixon[84,85] have used the method to study oxidation in both emulsified and solubilized oils of cosmetic interest. The effect of antioxidant activity and the concentration of peroxide present in a linoleic acid system have been studied by this method.[86] A detailed study of the accelerated oxidation of hemin in an emulsion at 45°C was made by Berner *et al.*[87] The antioxidant was added to the fat prior to emulsification and the oxygen uptake then measured. The effect of antioxidants was to increase the induction period. The age and purity of the hemin, pH and peroxide value of the fat and temperature all affect the induction period. The activity of BHA, propyl gallate, *tert*-butyl hydroquinone, tocopherol and synergists (EDTA, ascorbic acid and citric acid) were studied.

Spectrophotometry. Ultraviolet analysis was first used by Mitchell[88] and the method was improved and extended. The fatty acids with conjugated unsaturation absorb at 230–375 nm with diene unsaturation being at 234 nm and triene at 268 nm. Chipault and Lundberg[89] found a direct relationship between peroxide value and ε at 232·5 nm.

Of possibly more value is infrared spectroscopy in that it may be used to identify hydroxyl, hydroperoxide, carboxy and many other groupings. However, the technique appears to have been little used for quantitative studies of peroxidation although Morris[90] has reviewed its application. The 3·0, 6·0 and 10·0 μm bands appear to be the principal regions involved and the principal use appears at the moment to be the determination of stereo isomeric changes during the course of the oxidation. The infrared spectra of some alkyl hydroperoxides are characterized by weak absorption in the 11·4–11·8 μm region.[91]

Choice of Antioxidant

The ideal antioxidant should be stable and effective over a wide pH range and be soluble in its oxidized form, and its reaction compounds should be colourless and odourless. Other obvious and essential requirements are that it should be non-toxic, stable and compatible with the ingredients in the products and their packages.

The list of effective antioxidants permitted in the USA for use in foodstuffs includes the materials shown in Table 37.2.

Table 37.2 Effective Antioxidants for Foodstuffs Permitted in the USA

Guaiacum resin
Tocopherols
Lecithin
Propyl gallate
Butylated hydroxyanisole (BHA)
Butylated hydroxytoluene (BHT)
Trihydroxybutyrophenone
Ascorbic acid
Ascorbyl palmitate
Monoisopropyl citrate
Thiodipropionic acid
Dilauryl thiodipropionate

Phenolic Antioxidants

Guaiacum Resin

Guaiacum resin is largely phenolic in character, but is a less effective antioxidant than most of the other phenolics mentioned above. It is more effective in animal than in vegetable oils and possesses an advantage over some other antioxidants in that it is equally effective in the presence and absence of water and it is not seriously affected by heating.

Nordihydroguaiaretic Acid

NDGA shares many of the properties of guaiacum resin but is more effective weight for weight. Higgins and Black[92] summarize their studies on the protection of lard with NDGA as follows: pure lard of low initial peroxide value was protected against development of oxidative rancidity by 0·003 per cent of NDGA, compared with the requirement of 0·006 per cent of propyl gallate. The stabilizing effect was proportional to the antioxidant concentration over the range of 0·003–0·03 per cent. A synergistic effect occurred with 0·003 per cent NDGA and 0·75 per cent citric acid. This, of course, arises from the sequestering effect of citric acid on heavy metals. NDGA is soluble in fats at levels up to about 0·05 per cent at 45°C and does not crystallize out very much on cooling. It was removed from the US permitted list in 1968.

Tocopherols

These natural materials are not widely used in practice because of their high price. They have some antioxidant effect with animal fats such as tallow and with distilled fatty acids, particularly in the presence of a synergist such as citric acid, lecithin, or phosphoric acid, but are of little value for the preservation of vegetable oils. Issidorides[93] has shown that the action of citric acid with tocopherols is not only a sequestering effect, but derives also from regeneration of the tocopherol in the reduced state. Sisley[94] gives a method for obtaining tocopherols mixed with lecithin as a synergist by extracting wheat germ oil with dichloroethylene.

Gallates

Gallates constitute one of the most important classes of antioxidants. The propyl ester is the only one permitted in foodstuffs in most countries but methyl, ethyl, propyl, octyl and dodecyl gallates are commonly used in cosmetics. Gallic acid itself is a powerful antioxidant, but tends to turn blue in the presence of traces of iron.

The valuable antioxidant properties of the esters of gallic acid have been described by many investigators. Boehm and Williams[95] found that for practical and commercial considerations of ease of solubility at low temperatures, acidity and colour, and from the point of general effectiveness, normal propyl gallate (that is, normal propyl-3,4,5-trihydroxybenzoate) was the outstanding antioxidant amongst the gallic acid esters investigated. These workers found that the protection afforded by 0·1 per cent of the normal propyl gallate in lard was equal to that obtained by ten times as much Siam benzoin and probably greater than that of thirty times as much Sumatra benzoin. Peredi[96] showed a tenfold increase in storage time of lard in the presence of 0·01 per cent of propyl or ethyl gallate. However, Tollenaar[97] suggests that gallates are not suitable for the antioxidation of vegetable oils.

Further recommendation of the esters of gallic acid has been given by Stirton, Turer and Riemenschneider.[98] They compared the antioxidant activities of *nor*dihydroguaiaretic acid (NDGA), propyl gallate, benzyl hydroquinone, alpha-tocopherol and their synergistic combinations with citric acid, *d*-iso ascorbyl palmitate and lecithin in a number of fat substrates: methyl oleate, methyl linoleate, methyl linolenate and the distilled methyl esters of lard. *Nor*dihydroguaiaretic acid and propyl gallate surpassed the other substances in antioxidant activity. Citric acid showed marked synergism with each antioxidant; the most effective combinations were those of citric acid with *nor*dihydroguaiaretic acid and with propyl gallate.

The possible toxicity of ethyl gallate has been thoroughly investigated, and no symptoms of toxicity have been observed in mice which received, orally or subcutaneously, massive doses of ethyl gallate, in concentrations far greater than could ever be approached by human beings when receiving foods stabilized against oxidation by the ester.[99]

Boehm and Williams[95] report that 0·5 g of propyl gallate was administered orally to one of them on six consecutive days. An examination of the urine during this period, and for a further six days, showed that no albumen was present, abnormal sedimental contents were not observed, there being a complete absence of red blood corpuscles and casts of any kind. They also cite pharmacological tests received from the Pharmacological Laboratories of the College of the Pharmaceutical Society (University of London) which concludes as follows:

1. Normal propyl trihydroxybenzoate is less toxic than pyrogallol, when administered orally to mice (acute tests).
2. There are no acute skin effects observable when a 10 per cent solution of normal propyl gallate in propylene glycol is left in contact with shaven guinea-pigs for 48 hours, or the human skin for 24 hours. This contrasts favourably with the erythematous effect produced under similar conditions by a 10 per cent solution of pyrogallol in propylene glycol.

Williams[100] gives solubilities of gallates in various oils (Table 37.3).

Table 37.3 Solubilities of Gallates in Various Oils at 20°C

	Almond oil (%)	Castor oil (%)	Mineral oil (%)	Groundnut oil (%)
Gallic acid	—	—	—	0·01
Methyl gallate	0·30	—	—	—
Ethyl gallate	0·40	—	—	0·01
Propyl gallate	2·25	22·0	0·5	0·05
Octyl gallate	3·00	18·0	0·005	0·30
Dodecyl gallate	3·50	21·0	0·01	0·40

Mixtures of octyl and dodecyl gallates with BHT and BHA (see below) have been recommended for fat stabilization by Peereboom[101] and in general it may be said that propyl gallate at a level of 0·01–0·1 per cent is superior to equal amounts of NDGA, tocopherol, guaiacum resin, sesamol, lecithin, or hydroquinone for the preservation of vegetable fats. Gearhart[102] showed that propyl gallate gave greater protection in the presence of BHT.

Butylated Hydroxyanisole (BHA)

BHA consists mainly of two isomers, 2- and 3-*tert*-butyl-hydroxyanisole. It is seldom used alone, as its activity in most systems is less than that of propyl gallate, but it forms a number of very useful synergistic mixtures with the gallate esters. Thus a mixture of 20 per cent BHA, 6 per cent propyl gallate, 4 per cent citric acid, and 70 per cent propylene glycol is commonly used in both the food and cosmetic industries. If such a mixture is used at levels of about 0·025 per cent total antioxidant, most animal and vegetable oils can be protected, as can the fatty esters such as methyl oleate.

Olcott and Kuta[103] have observed an interesting synergistic effect with BHA and amines such as octadecylamine, tri-iso-octylamine, and proline. No synergistic effect was found with BHT. Proline was particularly useful in the treatment of vegetable oils.

Butylated Hydroxytoluene (BHT)

BHT is 2,6-di-*tert*-butyl-4-methylphenol, sold as BHT by Kodak Chemical Co., as Topanol O and OC (purified grade) by ICI, and as Ionol and Ionol CP by Shell Chemical Corporation. It may also be called di-*tert*-butyl-*p*-cresol, DBPC.

BHT is widely used as an antioxidant for fatty acids and vegetable oils, and possesses several advantages over the other phenolic antioxidants in its freedom from any phenolic smell, its stability towards heating, and its low toxicity. It was approved for use in foods in the USA in 1954, at levels not exceeding 0·01 per cent. Normally, in cosmetics containing unsaturated materials, a level of 0·01–0·1 per cent should be used, with addition of a suitable sequestering agent such as citric acid or EDTA. BHT is not synergized by gallate esters.

Auto-oxidation of fatty materials takes place with a logarithmic velocity coefficient, so that it is important to stop such oxidation as early as possible in the life of a material. Some manufacturers of fatty acids, etc., will now supply their products with BHT or other suitable antioxidants already added, so that oxidation is checked immediately after manufacture.

Trihydroxybutyrophenone

Knowles *et al.*,[104] report that some of the 2,4,5-trihydroxyphenones, especially the butyrophenones, have outstanding effects with lard, groundnut oils, and tallow. Although the product is a recognized food additive in the USA, it does not appear to be widely used in the cosmetics industry.

Non-phenolic Antioxidants

Many non-phenolic antioxidants are chelating agents. Ascorbic acid and ascorbyl palmitate appear to act by stopping the free-radical oxidation process.

Ascorbyl esters are particularly effective in vegetable oils, and make an excellent synergistic mixture with phospholipids such as lecithin and tocopherol.[105]

Among the sequestering agents, the thiodipropionates are widely used, usually in conjunction with phenolic antioxidants. The esters of fatty alcohols have greater solubility in oils.

Monoisopropyl citrate has similar sequestering action to citric acid itself, but a greater fat solubility.

Lecithin is an effective synergist for many phenolic antioxidants, mainly because it is an oil-soluble phosphate with excellent sequestering properties. Members of another class of oil-soluble sequestering agents are MECSA (mono-octadecyl ester of carboxymethylmercapto-succinic acid) and METSA (mono-octadecyl ester of thiodisuccinic acid). Under some conditions these materials can function as effective antioxidants in concentrations as low as 0·005 per cent—see the review by Evans *et al.*[106] They possess the disadvantage that they decompose on heating, and must therefore be added, like perfume, during the cooling phase of manufacture.

In general, the effect of any true (that is, chain-stopping) antioxidant can be enhanced by the proper choice of a suitable sequestering agent to slow down the initiation of chain reactions at the outset. Citric, phosphoric, tartaric and ethylenediamine tetra-acetic acids should always be considered as possible additives to a system that is insufficiently protected against oxidation, before including more phenolic material. The use of such sequestering agents is cheaper, and it is less likely to lead to discoloration or odour development, than the use of high concentrations of phenols. Of the phenolic materials, BHT is probably the most universally useful, but each system has its peculiarities which must be studied at first hand.

Photo-deterioration

Another form of deterioration sometimes encountered is that caused by light in the visible or the UV spectrum. Such photo-deterioration generally manifests itself as fading of the colour of the product or development of off-colours.

Packaging in opaque containers or wrappers so as to exclude all light is, of course, an obvious way to avoid this type of deterioration, but this is not always desirable, nor even necessary. It is frequently possible to wrap or pack in transparent material suitably coloured or containing a UV absorber to screen out the offending portions of the spectrum. In some cases where UV energy is causing the deterioration, the UV absorber can be incorporated in the product. Mecca was reported[107] as having found that uric acid at 0·02–0·5 per cent would protect solutions coloured with FD&C Blue No.1, D&C yellow No.10, FD&C Green No.8 and cochineal, exposed to direct sunlight, while control solutions without uric acid were completely bleached.

UV-induced deterioration frequently involves the presence of traces of metals, particularly iron, and when this is the case the screening agent may be reinforced, or in some cases replaced, by a chelating agent such as ethylenediamine tetra-acetic acid (EDTA). The permeability of the cell walls of some bacteria, notably the Gram-negative *Pseudomonas aeruginosa*, is altered by EDTA; Smith[108] has found that the addition of concentrations in the region of

0·05 per cent greatly enhances the antibacterial potency of phenolic antiseptics. Small amounts of this material might thus serve two useful purposes in protecting systems prone to deterioration by UV and susceptible to the omnipresent *Pseudomonas* species.

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Chapter Thirty-eight

Emulsions

Introduction

Every cosmetics laboratory worker knows that emulsions are relatively stable mixtures of oils, fats and water and are made by mixing oil-soluble and water-soluble substances together in the presence of an emulsifying agent. Emulsions—creams and lotions—form a very important part of the cosmetics market; much time is spent in the development of new raw materials by both suppliers and cosmetics companies. Formulae for good, stable cosmetic emulsions are available from books or suppliers' literature and it is not difficult for even a novice laboratory technician to make a satisfactory emulsion by following simple written instructions. Clearly, however, no cosmetics chemist can consider himself competent until he understands how to formulate emulsions of his own and how to incorporate into them certain desired characteristics. In order to do this, he must learn something of the fundamentals of emulsion technology. How far this is pursued will depend upon the inclinations of the individual, but the aim of this chapter is simply to provide a sufficiently detailed account of these fundamentals to allow the reader to experiment for himself with understanding and to form ideas of his own. More detailed information can be obtained from the references cited at the end of the chapter.

Basic Principles

The starting point in this study is the recognition that certain substances show an 'affinity' for each other and others do not. A simple illustration of this point is that water and ethanol are completely miscible. Their molecules are quite happy to exist side-by-side together and show no tendency to separate into discrete areas populated largely or exclusively by their own kind. These two materials show an 'affinity' for each other which is obviously not shared by (say) mineral oil and water. This idea of 'affinity' plays an important part in emulsion technology and has to do with the manner in which individual molecules appear to attract their neighbours in a given environment. Molecules of the same substance—for example, water—exert an attractive influence on each other and were it not for the fact that under normal circumstances each molecule is in turn attracted by many others around it in all directions, any two molecules might be pulled together. This phenomenon is called 'cohesion' and the force of cohesion between molecules is attributed to their 'cohesive energy'. The magnitude of these cohesive forces depends not only upon the size of the molecules taking part but also upon their chemical make-up. The basic principle is that 'like attracts like'. Related molecules such as water and ethanol show no tendency to separate because the cohesive forces between water and ethanol molecules are similar in magnitude to those between water and water or ethanol and ethanol. When mineral oil is introduced into water, however, the cohesive forces between water and mineral oil are negligible compared with those between the molecules of the two materials themselves, and separation rapidly occurs.

'Affinity' manifests itself not only as solubility but also in the concept of the 'phase'. When two or more materials in contact with each other co-exist as overtly different and separate entities, each is referred to as a 'phase' (Table 38.1). In two-phase systems one phase may be distributed as a large number of distinct and separate entities in the other. Under these circumstances, the former is known variously as the 'internal', 'disperse' or 'discontinuous' phase and the latter as the 'external' or 'continuous' phase. When one material is dispersed in a finely divided state within another in this way, the area of contact between the two phases is exceedingly large. It is not surprising, therefore, that many of the characteristics exhibited by such a system depend primarily on the chemical or physical natures of the two surfaces and the interaction between them. This is certainly true of cosmetic emulsions.

Table 38.1 Some Common Two-phase Systems

Continuous phase	**Disperse phase**	**System**
Gas	Solid	Smoke
Gas	Liquid	Aerosol
Liquid	Gas	Foam
Liquid	Solid	Dispersion
Liquid	Liquid	Emulsion
Solid	Gas	Foam

Properties of Surfaces

In general, the outermost layers of materials exhibit very different properties from the bulk, this being entirely due to the environment in which the surface molecules find themselves. In Figure 38.1, A represents a molecule some way in the interior of a liquid. A is surrounded by other molecules which, if close enough, exert an appreciable attraction on it. These will be contained in a sphere, centre A, with a very small but finite radius (represented in the figure by an exaggerated dotted line around A)—the 'sphere of molecular activity'. Since there are as many molecules attracting A in any one direction as attract it in the opposite direction, there is no resultant cohesive force on A. This is far from true of a second molecule, B, situated in the liquid surface. Here, forces of attraction below B are not precisely cancelled out by the attraction of other molecules above it and a resultant force *F* is exerted on B, tending to pull it into the interior of the liquid. (It should be emphasized that B is very close to the surface and that Figure 38.1 is greatly exaggerated for clarity.)

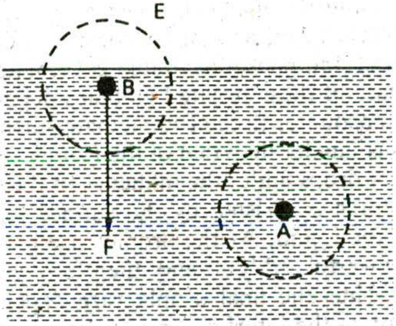


Figure 38.1 Molecular explanation of surface tension

This same consideration applies to all surfaces, whether gas, liquid or solid, although it is in gases and liquids, in which the molecules have considerable mobility, that its effect is clearly seen in determining the shape of the material. Since the inward forces on the molecules in a liquid surface tend to make the molecules move towards the interior, the surface tends to contract and become as small as possible, so that the surface area will be the minimum for a given volume of liquid. Since a sphere is the shape which has the minimum surface area for a given volume, if no other forces were acting on the liquid, it should be expected to assume a spherical shape. Relatively large masses of liquid are subject to proportionately large gravitational forces; for this reason they will assume the shape of any retaining vessel (for example, a beaker or measuring cylinder). For very small masses, however, such as may be found in droplets of internal phase in cosmetic emulsions, gravitational forces play a relatively minor role and the droplets may be spherical to a high level of approximation.

Because of the inward resultant force on surface molecules, all surfaces are said to possess 'surface tension' and the magnitude of the surface tension depends on *F*. Of course, if the molecules of material above the surface of the liquid have little or no measurable attraction for B, then the magnitude of *F* depends primarily on the properties of the liquid itself. Should the air, gas or solid above the liquid surface show some affinity for B, then *F* and the surface tension will be lower. Each surface is a boundary or interface whose characteristics, including the surface tension, depend upon the influence of the materials on both sides.

Principles of Emulsion Stability

It is a very commonplace observation that an oil and water mixture can be emulsified by shaking. The more vigorous the shaking, the finer the size of the droplets of dispersed phase. Sooner or later, however, the droplets of dispersed phase become noticeably larger as they coalesce until the initial two layers are re-formed ('phase separation'). It is important to understand the reasons for emulsification and for coalescence. There are two complementary ways of describing these phenomena, both of which will be discussed briefly. One viewpoint is mechanical and the other thermodynamic; they are equally important.

Mechanical Model of Emulsification Coalescence

When a quiescent mixture of oil and water consisting of two simple layers is shaken, large volumes of one phase inevitably get isolated and trapped within the other phase. The fate of these isolated globules depends partially upon the turbulence which they encounter in their immediate surroundings. If the size of the local eddy currents is smaller than that of the globule, the latter will break up into a number of smaller drops under the influence of the shear force exerted by the eddy. This shear force is resisted by the surface tension at the interface between the drop and the liquid. As the droplet size becomes reduced it must find smaller, more powerful eddys—and therefore greater turbulence—to become even smaller. Thus the final droplet size depends almost exclusively upon the surface tension at the interface and the degree of turbulence set up in the continuous phase.

Even while the droplets of dispersed phase are being broken up, however, they are simultaneously coalescing. The coalescence process can be considered in a number of stages. Firstly, the droplets must have sufficient mobility to move through the continuous phase to find each other. When they do bump into each other, very few collisions result in immediate coalescence. The thin film between two colliding droplets may cause them to rebound. If they do not, they may adhere to each other; this is the next essential stage in the process and is sometimes referred to as 'aggregation' or 'flocculation'. Finally, the intervening film of continuous phase must drain away to the point where it can rupture, allowing the contents of the two drops to combine to form a larger droplet with a smaller total surface area.

The rate of coalescence is determined by the slowest of these processes. If the viscosity of the external phase is high and the total volume of internal phase low, then the low mobility of the scattered drops of dispersed phase may wholly determine the rate of coalescence. If the droplets of internal phase are uniformly small, adhesion may determine the coagulation rate. The forces governing collision and adhesion for liquid droplets are the same as for those governing solids suspended in liquids or in other solids. The ease of adhesion increases with the particle size of the largest of the two adhering entities—thus a few large globules in an emulsion of otherwise small droplet size can markedly increase the rate of coalescence. When clumps of aggregated internal phase either rise to the top or fall to the bottom of an emulsion, the effect is often called 'creaming'. At this stage, further agitation can re-disperse these aggregates and rescue the emulsion. Once the aggregates have coalesced, however, and phase separation has occurred, re-formation of the emulsion is made more difficult. It is often pointed out that the rate at which particles sink or float in liquids—whether they be single particles or agglomerates—is predicted by Stokes's Law, one form of which is as follows:

$$K = \frac{2}{9} \cdot g \cdot \frac{r^2(d_1 - d_0)}{v}$$

where K is the terminal velocity of a sphere, radius r and density d_1, falling through a liquid of density d_0 and viscosity v. Although Stokes's Law can apply only very approximately to most emulsions, it does serve as a very simple model for the movement of internal phase droplets through the external phase.

Thermodynamic Description of Emulsification and Coalescence

When the surface area of a liquid is increased (for example, by agitation), molecules from the interior rise to the surface. They do so against the force of attraction of neighbouring molecules and hence some mechanical work or energy is always required to increase the surface area. The surface also tends to become cooled and thus heat flows into it from the surroundings. Hence there is an increase in surface energy equivalent to the sum of mechanical energy expended and the heat energy absorbed. The relationship between the increase in surface energy, ΔS, associated with an increase in surface area, ΔA, is as follows:

$$\Delta S = T \,.\, \Delta A$$

where T is the interfacial surface tension between the liquid and its surroundings. Thus it can be seen that surface tension is no more than the increase in surface energy associated with a unit increase of surface area.

It is a well-known principle in mechanics that an object is in stable equilibrium when its potential energy is at a minimum. Given the opportunity, therefore, the emulsion will lose its considerable energy excess to its surroundings in the form of heat by coalescence of the droplets of internal phase and phase separation.

Stabilization of Cosmetic Emulsions

The problem facing the cosmetic formulator, having decided upon an emulsion, is how to prevent this thermodynamically unstable system from separating into layers. Based on the considerations of the last few paragraphs, the following recommendations can be made.

(a) By increasing the viscosity of the external phase, he will decrease the mobility of internal phase droplets making it more difficult for them to collide with each other.
(b) By ensuring that the internal phase is of the smallest and most uniform drop size possible, he will decrease the likelihood of adhesion between two drops.
(c) By increasing the mechanical strength of the interface, he will make this less susceptible to rupture with the resulting coalescence of adhering drops.
(d) By decreasing the surface tension, he will decrease the thermodynamic 'driving force' for coalescence.

It should be noted that the increase in stability which results from the formation of internal phase droplets of very small size represents an apparent anomaly. It has already been shown that decreasing the droplet size causes a rapid increase in surface area and also that a large surface area can only be achieved, in a given system, by a larger energy input. Such a system should therefore possess a high excess energy content—which seems to be in conflict with the rule about high energy systems being less stable than those of low energy content. Apparently, therefore, the stabilizing effect of a low probability of adhesion between internal phase droplets far outweighs the influence of excess free surface energy in bringing about coalescence.

Surfactants and Emulsifiers

Returning to the recommendations listed above, it can be seen that suggestions (c) and (d) relate directly to the interface between the droplet of internal phase and its environment. Although the effect was discovered by accident (well before the theories of chemistry and physics had been developed), it has proved possible to stabilize emulsions by providing a physical barrier at the interface which not only reduces the likelihood of its rupture but which may actually prevent droplets from touching each other while at the same time making emulsification easier by reducing the interfacial surface tension. The possibility of finding materials which will migrate and live in an oil–water interface stems from the idea of chemical affinity; all that is necessary is that at least part of the material should show an affinity for oil and part for water (although neither affinity must be strong enough to overwhelm the other). Any such materials would be bound to migrate to the interface in order to satisfy these predispositions—and so, apparently, they do. Inevitably, materials which possess these characteristics have been called '*surface-active agents*' and this has been shortened to 'surfactant', a word which may be used either as a noun or as an adjective. Surfactants have a large number of uses in industry other than in the formation and stabilization of cosmetic emulsions; they may be used, for example, as solubilizing, wetting or spreading agents. These functions are all related to their role in emulsification but when designed and used for the latter purpose they should be referred to as emulsifying agents or 'emulsifiers'.

Cosmetic emulsions are almost invariably stabilized with emulsifiers and may be thought of as 'oil-in-water' (with water as the continuous phase) or 'water-in-oil' (where water is the internal phase). With very few exceptions, such a simple picture is only very approximate since the two phases will have some mutual affinity for each other, causing the probable formation of other phases of intermediate composition. However, for the sake of clarity the oil-in-water and water-in-oil models will be adopted in subsequent discussion. It is important to appreciate, however, that even these crude emulsion systems can no longer be considered to consist of two phases once the emulsifier has been added (although, regrettably, this error is often committed). The interface, containing the emulsifier, must now be regarded as a third phase.

Figure 38.2 illustrates the same liquid surface described in Figure 38.1 but now a thin layer of surfactant, S, has occupied the interface. The affinity of S for the surface molecule B is much greater than that of the original environment, E, and

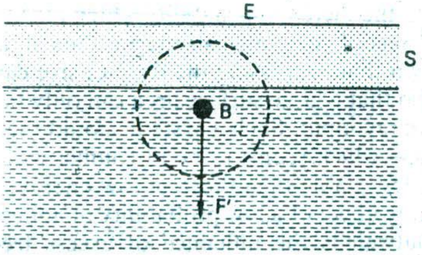


Figure 38.2 Reduction of surface tension by a surfactant

the resultant inward force, F', is less than before. The surface tension between the liquid and S is therefore lower than that between the liquid and E. This is referred to as 'a lowering of surface tension between the liquid and E', although we can see that this is not strictly accurate. At the same time, the surface tension between S and E is lower than that between the liquid and E for similar reasons.

Types of Emulsifier

Such is the number and variety of emulsifying agents now commercially available that their classification must be considered a daunting task—indeed, there are manuals devoted exclusively to it. Fortunately, the problem of choosing from among the bewildering variety of products is made easier by the classification of emulsifiers according to their chemical type and their mode of action.

Before proceeding to describe the emulsifier types of major commercial importance, however, a distinction should be made between these (which function at a molecular level) and certain finely divided solids which have also been shown to exhibit emulsion-stabilizing properties. Such solids undoubtedly function by migrating to the emulsion interface, forming a barrier against coalescence: it follows that the surface of such solids must not be predominantly water-wettable (hydrophilic) or oil-wettable (lipophilic). Such powders have little value as cosmetic emulsifiers but since many cosmetic emulsions also contain suspended powders (liquid foundations, for example) it is as well to bear in mind that these could possibly play some part in deciding the stability of the product.

Figure 38.3 is a diagrammatic representation of a molecule of the more conventional type of surfactant. The molecule can be considered as being composed of two parts—a water-loving or hydrophilic group at one end (H) and an oil-loving or lipophilic group at the other end (L). Since the lipophilic group is usually a hydrocarbon chain, it is often represented diagrammatically as a 'tail' as in Figure 38.3. It is easy to see how such a molecule would behave if dispersed in a single liquid: in Figure 38.4a, the surfactant has been dispersed in oil. Since the cohesive forces between the hydrophilic portion of the molecule and the oil molecules is negligible compared to those between hydrophilic ends of the molecules among themselves, the molecules orientate as indicated in clusters or 'micelles'. The lipophilic parts of the surfactant molecules, experiencing comparatively large cohesive forces from the oil molecules, are happy to extend outwards into the oily environment.

Figure 38.4b indicates the opposite orientation, encountered when the same molecules are dispersed in water or hydrophilic media. The same rules apply here as before except, as would be expected, it is the lipophilic ends of the

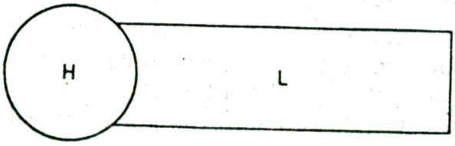


Figure 38.3 Surfactant molecule

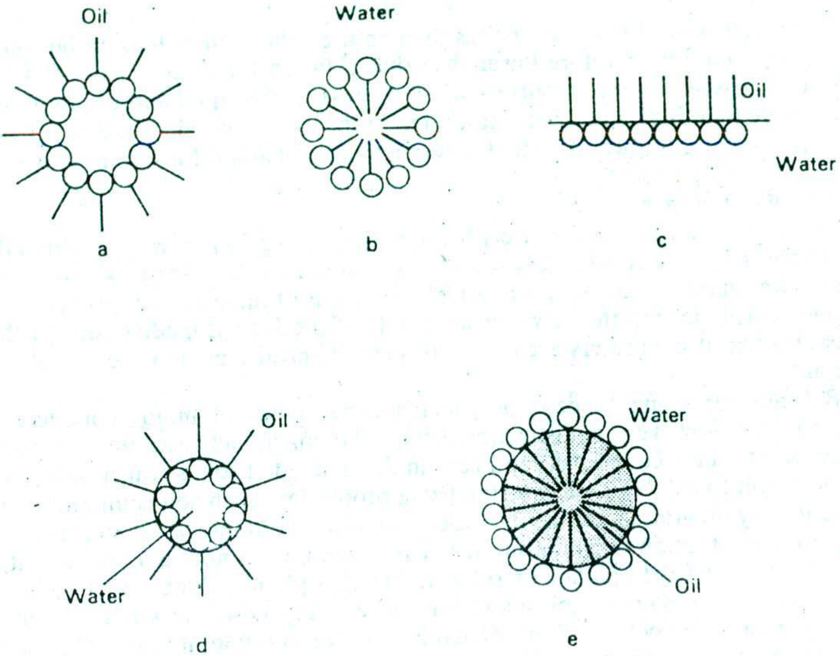


Figure 38.4 Behaviour of surfactants in various environments

molecule which cluster closely together in order to escape from the watery environment.

In Figure 38.4c oil has been added to the water and, as expected, the surfactant has migrated to the interface. If now an emulsion is formed, each spherical internal phase droplet will be covered with orientated surfactant molecules. (Figure 38.4d illustrates a water-in-oil and Figure 38.4e an oil-in-water emulsion.)

It is easy to verify, by experiment, that such interfacial surfactant layers can stabilize emulsions and this is primarily because the interface is made less liable to rupture. To understand this more clearly, however, it is first necessary to examine the chemistry of surfactants in greater detail.

Classification of Emulsifiers

There is only a limited number of chemical variations which can be played on the surfactant theme. Those relating to the lipophilic end of the molecule (or, at least, the more important of them) are as follows:

1. Variation in the hydrocarbon chain length.
2. Degree of unsaturation of the hydrocarbon chain.
3. Degree of branching of the hydrocarbon chain.
4. The introduction and juxtaposition of aryl groupings in the hydrocarbon chain.

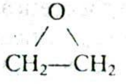
For the hydrophilic end of the molecule the following variations are possible:

1. Introduction of ionizable anionic end groups.
2. Introduction of ionizable cationic end groups.
3. Introduction of amphoteric groups.
4. Introduction of other water-soluble but 'nonionizing' groups such as hydroxyl or ethoxyl.

All these variations have been used in practice and the classification of surfactant type depends, customarily, only upon the nature of the hydrophilic end of the molecule. Emulsifiers may thus be 'anionic', 'cationic', 'amphoteric' or 'nonionic'.

Hydrophilic–Lipophilic Balance of Surfactants

It is rarely the case that the affinity which the lipophilic end of the surfactant molecule has for the oil phase is equal to the affinity which the hydrophilic end of the molecule has for the aqueous phase. Clearly, the ratio of these affinities should play an important part in deciding the performance of the emulsifier in an emulsion system, and it is therefore fortunate that a relatively simple means of assessing this balance is available—at least, for certain emulsifier types. The fundamental point is that water-wetting or oil-wetting power seems to be a colligative property of certain atoms or chemical groups in the surfactant molecule. In other words, these entities contribute to wettability in a predictable way so that the value of each one may be added to the whole in order to obtain a composite value. For example, in nonionic emulsifiers consisting of alkyl chains coupled to polyoxyethylene chains, each oxygen atom is equivalent in water-wetting power to the oil-wetting power of three CH_2 groups. One ethylene oxide group ($—CH_2 . CH_2—O—$) is thereby balanced by each $—CH_2—$ group in the alkyl chain. This important point is illustrated by reference to the following generalized formula for the condensation products of ethylene oxide and stearyl alcohol, namely polyethylene glycol ethers of stearyl alcohol:



ethylene oxide

$CH_3(CH_2)_{16}CH_2OH$ stearyl alcohol

$CH_3(CH_2)_{16}CH_2 \vdots (OCH_2CH_2)_nOH$ polyethylene glycol ethers of stearyl alcohol

(n varies between 2 and 30 in most commercial forms). The dotted line indicates the 'balance point' of the molecule, the groups to the left being oil-soluble and those to the right being water-soluble. Counting each $—CH_2—$ group or $—CH_3—$ group as unity, the lipophilic end of the molecules adds up to 18 and the hydrophilic end to $3 + n$ ($O = 3$; $—CH_2CH_2O— = 1$). If n is less than 15, therefore, the lipophilic tendencies of the molecule outweigh its hydrophilic properties, while at values of n greater than 15 the reverse is true. Moreover, the greater the difference in numerical value between the two sides, the greater the imbalance in the relative affinity for the two phases exhibited by the molecule.

The hydrophilic–lipophilic balance is an important property of the emulsifier since it determines the type of emulsion it tends to produce. The simple colligative nature of this phenomenon as applied to nonionic emulsifiers led the Atlas Chemical Company (as it then was) to devise a linear scale which enables the overall balance of each emulsifier to be expressed as a single number—the HLB (hydrophilic–lipophilic balance) number.[1] This is merely the weight per cent of the hydrophilic content of the molecule divided by an arbitrary factor of 5. Thus if a nonionic emulsifier were 100 per cent hydrophilic (which, of course, is impossible) it would have an HLB value of 100/5 or 20. The HLB scale therefore stretches (in theory) from 20 for a completely hydrophilic molecule to 0 for a completely lipophilic one. In the case of the polyethylene glycol ethers of stearyl alcohol cited above, HLB would be calculated as follows:

Molecular weight of the lipophilic stearyl chain, $C_{18}H_{37} = 253$.

Molecular weight of the hydrophilic end of the molecule $= 44n$ (ethoxyl groups) + 17 (remaining oxygen and hydrogen).

If $n = 3$,

$$\text{total molecular weight} = 253 + [(44 \times 3) + 17]$$
$$= 253 + 149 = 403$$
$$\text{HLB} = \frac{149}{403} \times \frac{100}{5} = 7{\cdot}4$$

If $n = 20$,

$$\text{total molecular weight} = 253 + 897 = 1150$$
$$\text{HLB} = \frac{897}{1150} \times 20 = 15{\cdot}6$$

The HLB value can only be determined in this simple way for nonionic emulsifiers of known and definite composition. The concept is also applicable to anionic or cationic emulsifiers, although it is possible to exceed the theoretical upper limit of 20 with these materials. This does not detract from the practical merits of the HLB system, but it does mean that alternative methods of determining HLB values have to be used. This will be described later.

Figure 38.5 summarizes the applications of surfactants of various HLB values.

Stabilizing Influence of the Surfactant Phase at the Interface

In Figure 38.2 it was seen that the interfacial film of surfactant—the third phase of a stabilized emulsion—produced two new interfacial surface tensions, one between the surfactant, S, and the original liquid (which we now identify as the water phase) and one between S and E, the environment outside the water phase, which now corresponds to the oil phase. For clarity, these new surface tensions will be designated T_{ws} and T_{so} respectively. Clearly, since both of these tensions depend upon the affinity of the appropriate ends of the orientated surfactant molecules for their watery or oily environment, the ratio T_{so}/T_{ws} is directly related to the HLB value of the surfactant. If the HLB is high (greater

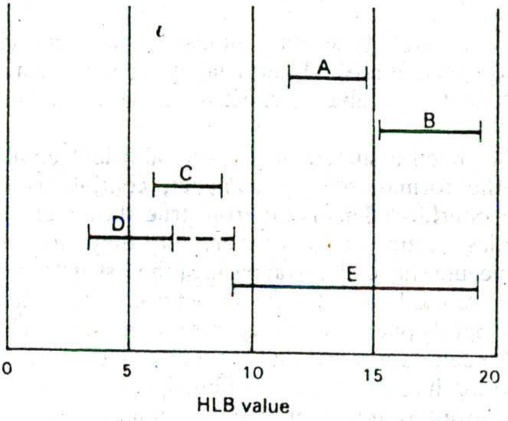


Figure 38.5 Practical applications of surfactants of various HLB values
A Detergents
B Solubilizers
C Surface wetters
D Water-in-oil emulsions
E Oil-in-water emulsions

than 10), then T_{so} is larger than T_{ws}. Remembering that the net inward force, F, on molecules in a surface is directly proportional to the interfacial surface tension, the surfactant surface has a propensity to curve towards the side having the greater surface tension—in this case, towards the oil phase.[2,3] With mechanical agitation, therefore, such a system would produce overwhelmingly an internal phase of oil dispersed in water. For surfactants having a low HLB value, exactly the reverse is true and a water-in-oil emulsion is the most probable end result.

Thus it can be seen that the relative lowering of the surface tension on each side of the surfactant interface helps to determine the nature of the emulsion and the ease of emulsification. It does not, however, determine the stability of the emulsion—this is a point which deserves great emphasis. The essential factors governing the integrity of the interfacial film and its resistance to rupture are its extension, its compactness and its electrical charge.[4] A lowering of interfacial tension is not vital for the stability of an emulsion.

Factors Contributing to the Strength of the Interfacial Surfactant Film

Perhaps the most obvious requirement is that there must be sufficient emulsifier present to form at least a monolayer over the surface of the internal phase droplets—and this, in turn, will depend upon the droplet size.[5,6] It is easy to verify in the laboratory that even the most stable cosmetic emulsion can be rendered unstable by progressive reduction of the quantity of emulsifier used in its production. Indeed, stability can usually be improved by a certain excess of emulsifier over this essential minimum. Evidence exists[7] that when there is a danger of a break in the interfacial film, the interfacial tension at the threatened point rises and signals to the reserve emulsifier molecules in the continuous phase that there is a fault. These spare emulsifier molecules close in and repair the damage. It appears that mixed interfacial films (films formed from more than one emulsifying agent), are able to resist breakage in this manner even more easily.[5]

Until now it has been assumed that, given sufficient emulsifier, there is no impediment to the formation of a compact, continuous film of emulsifier molecules in the interface. This is far from true, however. Not only do these identical molecules occupy a monolayer, but they are orientated so that neighbouring molecules have identical parts of their structure in close proximity. As a consequence of the balance of forces between like molecules at very close proximity, such a tightly packed monolayer is not thermodynamically stable, and the emulsifier molecules are constrained to remain separated from each other, so weakening the strength of the interfacial film. Where the hydrophilic ends of the molecules are ionized (anionic or cationic emulsifiers) this separation and weakening is further exaggerated by the repulsion of juxtapositioned like electrical charges.

The second effect tending to interrupt the continuity of the interfacial monolayer is simple steric hindrance. Consider, for example, the problem experienced by neighbouring molecules such as the polyoxyethylene sorbitan unsaturated esters indicated in Figure 38.6. Obviously it would not be easy for such molecules to pack closely together in an orientated monolayer. The importance of these steric effects can also be judged by the fact that whereas soaps of monovalent metal ions tend to form oil-in-water emulsions, the similar soaps with polyvalent metal ions produce largely water-in-oil emulsions. In this case, steric hindrance actually dictates the direction of curvature of the interface.

One way of overcoming these problems is to incorporate one or more additional species of emulsifier molecule into the interfacial film—in other words, to use a mixed emulsifier system. It is relatively simple to show, experimentally, that mixed emulsifiers produce more stable emulsions from a given oil–water mixture than single emulsifiers—provided only that the emul-

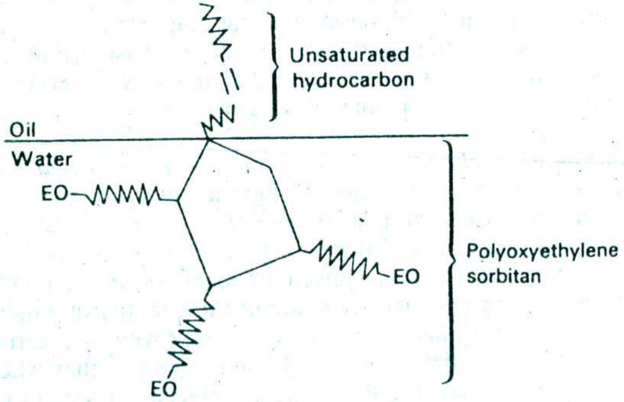


Figure 38.6 Oil–water interface showing orientation of a molecule of a polyoxyethylene sorbitan unsaturated ester

sifiers chosen are chemically and physically compatible with each other. The choice of a combination of anionic and cationic molecules, for example, would be unwise because of chemical combination and electrochemical neutralization of charges. This does not mean, however, that they have to be of similar HLB values. In fact, better results are often achieved by a combination of surfactant molecules having widely differing HLB values combined in such quantities as to produce a resultant HLB close to the optimum for the system to be emulsified (this latter point will be discussed more fully later).[8] The reason for this phenomenon is clearly that the two dissimilar molecular types can, by alternating in the interface, form a much more closely packed, condensed interfacial film. In Figure 38.7a the internal phase has been surrounded by an interface of surfactant molecules of low HLB value which, because of steric hindrance and the mutual repulsion of chemically identical entities, has formed only a discontinuous film. Figure 38.7b shows this surfactant partially replaced by two others with widely different HLB values and chemical composition allowing a close-packed, continuous film to be produced which acts as a much better mechanical barrier to coalescence. Sometimes the second emulsifier can have very little emulsifying potential at all—that is, it can have an HLB value close to zero—just so long as it can migrate to the surface and 'insulate' the other molecules from each other. Cetyl and oleyl alcohols will function in this manner and so will glyceryl monostearate.

Influence of Electrical Charge on Emulsion Stability

Consider an oil droplet stabilized with sodium stearate in an oil-in-water emulsion. The negatively charged carboxylate groups project outwards from the interfacial film into the water phase while the non-polar hydrocarbon chains enclose the oil droplet. Thus the presence of electrical charges at the surface of each droplet is explained and the mutual repulsion of like charges on all the droplets helps to prevent coalescence. The optimum stability conditions exist, not surprisingly, when the interfacial film is completely covered with charges.[5,6] It is also obvious that, since opposite charges will neutralize one another, the combination of anionic with cationic emulsifiers can only result in a decrease in the stability of the emulsion.

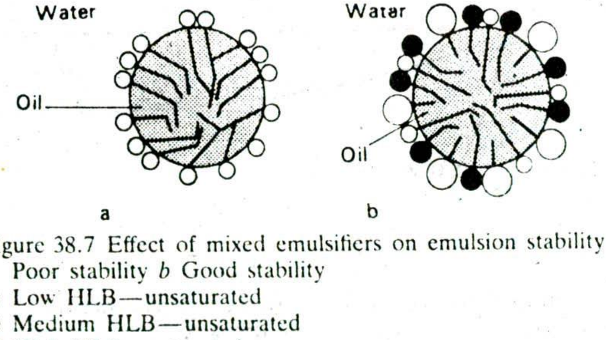


Figure 38.7 Effect of mixed emulsifiers on emulsion stability
a Poor stability *b* Good stability
○ Low HLB—unsaturated
● Medium HLB—unsaturated
◯ High HLB—saturated

More surprisingly, it has been shown that charges at the interface also occur when a totally nonionic emulsification system is used. This has been accounted for by frictional forces originating in the movement of oil droplets in the continuous phase. It has been shown that electrical charge can result when two liquids with different dielectric constants are mixed and that the one with the higher dielectric constant is always positively charged while the one with the lower dielectric constant is always negatively charged.[9] (Thus in oil-in-water nonionic emulsions, the oil droplets are always negatively charged.)

Although no method exists for measuring surface potentials in an emulsion directly, the 'zeta potential' can readily be evaluated by measuring the velocity of charged droplets in an applied DC field. The measured values of emulsion zeta potentials for nonionic emulsifier combinations have proved to be surprisingly high (about 40 mV); perhaps even more interesting is the fact that, when zeta potential is plotted graphically against the HLB of the emulsifier combination, the maximum zeta potential is always found to coincide with the optimum HLB value for the particular system studied.

If mobile ions are present in the external phase of an emulsion, they are attracted by the charged droplets of the internal phase (if these have an opposite charge) giving rise to the formation of an electrical double layer. The nature and effect of this double layer are markedly different in oil-in-water emulsions and water-in-oil emulsions (Figure 38.8).[10] The thickness of the double layer around oil droplets in oil-in-water emulsions amounts to only 10^{-3} to 10^{-2} μm. Electrical repulsion therefore occurs at very short inter-globular distances and this results in a very considerable electrical barrier which must be overcome before two droplets can coalesce. On the other hand, the electrical double layers around water droplets in oil are very diffuse (several μm in size) and the electrical potentials of adjacent droplets overlap, lowering the potential barrier. The stability of water-in-oil emulsions cannot, therefore, be attributed to electrical repulsion of charged droplets.[11]

Other Factors Affecting the Stability of Emulsions

It has been shown how the physical barrier afforded by the condensed molecular layer of emulsifiers at the interface of an emulsion can help to prevent coalescence and how this same layer can, by electric repulsion and steric

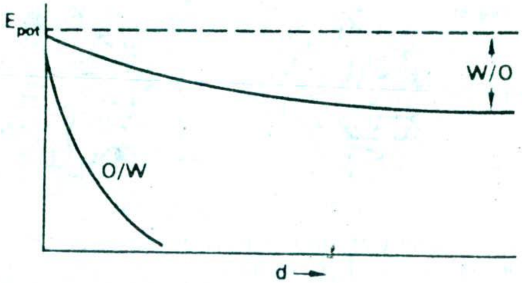


Figure 38.8 Potential energy (E_{pot}) of repulsion due to electrical double layers plotted against distance (d) between internal phase droplets

hindrance, prevent droplets coming together. Both these phenomena have a stabilizing influence on the emulsion but there are other factors which may also affect the stability for better or worse.

The simple picture given by Stokes's Law shows that mobility of internal phase droplets is affected by the viscosity of the continuous phase, the difference in density between the oil and water phases and the size of the disperse phase droplets. Of these, the differential density between the two phases is least amenable to experimental control, although it is obvious that the smaller this difference is, the less is the likelihood that the internal phase will float to the surface or sink to the bottom of the emulsion.

Viscosity of the Continuous Phase

Viscosity is an important parameter, because it can be readily varied—usually by the addition of a thickening or gelling agent (provided that these are compatible with the emulsifier system). Although a large number of such agents is available, the formulator is limited in his choice because the rheological behaviour of most emulsions is almost entirely determined by that of the external or continuous phase. Thus the viscosity, thixotropy and the 'feel' on application of the total emulsion may be affected by the thickener chosen for the continuous phase. The mode of action of many thickening agents is two-fold: firstly, by forming gels consisting of long, interlinked molecules, they physically hamper the flow of continuous phase and of particles of internal phase within it; secondly, they compete with the internal phase chemically for the available external phase. For example, sodium carboxymethylcellulose forms a gel-like dispersion in water, trapping free water and oil droplets within its interstices in oil-in-water emulsions. At the same time, the polymer chains absorb water and become swollen, so decreasing the amount of continuous phase available to the oil droplets. In the same way, free stearic acid (or simple complexes of it) will gradually crystallize in emulsions stabilized with sodium or triethanolamine soaps, resulting in a gel structure which gradually builds up over several hours after manufacture. If, moreover, excess cetyl alcohol over the quantity required to help form a condensed, monolayer interfacial film is present, this will increase the viscosity of the continuous phase by micelle formation, trapping water within each micelle and crowding the available continuous phase. In the same way, pigment suspensions can increase the continuous phase viscosity, although this is a rather special case since the degree of viscosity increase is also very dependent upon the surface characteristics of the pigments involved.

Ratio of Oil Phase to Water Phase

Although the proportion of oil phase to water phase has a marked effect on such parameters as the 'feel' and overall viscosity and appearance of the emulsion, it can also influence the stability. The higher the proportion of internal phase, the greater the number of droplets. The chances of collision are thereby increased and the average distance which one droplet must travel to collide with another (the 'mean free path') is reduced. All this increases the likelihood of coalescence.

Temperature

In has already been stressed that optimum stability is achieved by the correct choice of emulsifier combination. The chosen emulsifiers must be compatible, of correct HLB value and of correct chemical type. These last two characteristics are heavily dependent upon the relative solubility of the hydrophilic and lipophilic ends of the surfactant in the water and oil phases respectively. Solubility, however, is very temperature-dependent. It is unlikely that as the temperature of an emulsion changes, the relative solubilities of both ends of all its emulsifier system will change in strict proportion. In other words, HLB is to some extent a temperature-dependent property itself. Variation of temperature can therefore decrease the stability of an emulsion. This is obviously something which must be borne in mind when formulating products for differing climates. However, the stability of emulsions is often tested in the laboratory by storage at elevated and refrigerator temperatures (and sometimes by cycling between these two extremes) in the hope that such methods will give a rapid indication of the stability on prolonged storage at average temperature. Such a practice is highly questionable. The stability testing of emulsions is discussed more fully later in the chapter.

Concentration of Ions in the Water Phase

The dielectric constant of the oil phase of an emulsion is not great enough to allow any ionizable chemical species to dissociate to any great extent and it has already been seen that this reduces the stabilizing influence of any electrical double layer when oil is the continuous phase. Dissociation is an important factor in oil-in-water emulsions, however, not only because of the influence on ionic emulsifiers but also because of the effects of other soluble ionizable species in solution including hydrogen and hydroxide ions.

The pH value of emulsions is a parameter which is often discussed for a variety of reasons, not least because of its effect on stability. It is necessary to remind ourselves, however, that pH is a measure of hydrogen ion activity in an aqueous environment. Whether the term should strictly be applied to an oil-in-water emulsion is a moot point since the influence of the oil phase and emulsifiers on hydrogen ion activity is probably unknown. However, common usage dictates that the measurement of the pH of emulsions, when the continuous phase is aqueous, will continue. Under no circumstances can the concept of pH be applied when oil is the continuous phase.

Nevertheless, the influence of hydrogen ion concentration in oil-in-water emulsions is dramatic whenever an ionizable emulsifier system is used because of the change of species which can be brought about. Anionic emulsifiers are converted to non-ionizable salts in acidic media and the reverse is true of cationic emulsifiers. In both instances, water solubility and therefore all emulsifier activity can be lost. The effect of pH on amphoteric emulsifiers is less dramatic but obviously dictates whether the anionic or cationic form predominates.

The presence of other mobile ions in solution in the external phase also has an important influence. They are attracted by the charged droplets of the disperse phase, as we have seen. The zeta potential falls as more electrolyte is added and this can decrease emulsion stability. Even at relatively high electrolyte concentrations and zeta potentials close to zero, many emulsions remain stable. This must be due to steric stabilization and the mechanical barrier afforded by a good interfacial film.

Practical Aspects of Emulsifier Choice

Having now accounted for the stabilization of emulsions, it will be apparent that the cosmetic formulator has a large number of options to choose between when considering the composition of a new emulsion. Many of these questions will be settled by his brief—the purpose for which the emulsion is to be designed and the desirable properties it is to have. A detailed account of the influence of the oil-soluble or water-soluble components other than the emulsifier system is outside the scope of this chapter, so that our starting point in choosing a suitable emulsifier system must be that the compositions of both phases have already been chosen.

Probably the first question that needs to be settled is the chemical classification of emulsifier system to be used. This, in turn, can depend upon the content of the other two phases. If the product is to be alkaline, cationics should not be considered. It would be equally unwise to use an anionic emulsifier in an emulsion of low pH and, if electrolyte concentration in the aqueous phase is to be high, nonionics are the best choice. On the whole, members of this latter group are probably least affected by incompatibilities with the remainder of the formulation—apart from the well known ability of polyoxyethylene chains to deactivate certain preservatives. Unfortunately, complete guidance on the choice of emulsifier type is not possible because of the many and varied factors involved; the formulator must experiment for himself to gain good practical experience in order to be able to come to a quick decision.

Determination of Required HLB

The optimum or 'required' HLB value of the emulsifier system for a given composition of oil and water phases provides a useful starting point in the selection of emulsifiers which will give an emulsion of good stability. The determination of the optimum HLB value is based upon a series of practical experiments in which a set of emulsions is produced, identical in every way except for variation in the ratio of a pair of emulsifiers. These emulsifiers are a matched pair, one lipophilic and one hydrophilic, of known HLB values—for example, sorbitan monostearate (HLB 4·7) and polyoxeythylene sorbitan monostearate (HLB 14·9). These are mixed in ratio to give combined HLB values according to the formula.

$$\text{HLB} = xA + (1 - x)B$$

where x is the proportion of a surfactant having an HLB value of A and the other surfactant has a value of B. This is a straight-line relationship and can therefore be computed graphically. The HLB values of the series of mixtures are chosen to differ by an increment of 2 throughout the range bounded by values of the two emulsifiers chosen. In the example above, a range of 4·7, 6, 8, 10, 12, 14·9 might be considered. For each of the test emulsions, an excess of emulsifier (approximately 10 per cent of the weight of the oil phase) is used and all the emulsions are made in precisely the same way. Usually, one or more of the emulsions will give better stability than the others. Should they appear to be uniformly good, however, the experiments must be repeated using less emulsifier; more emulsifier should be used if the set is uniformly bad. Occasionally, two combinations having widely different HLB values show outstanding ability. In this case the low value probably relates to a water-in-oil and the high value to an oil-in-water emulsion. This trial-and-error process has now enabled the experimenter to arrive at an idea of the optimum HLB value for his system. At this stage, a more accurate determination can be achieved by producing a second set of emulsions using the same emulsifier pair but combined to give HLB values in smaller increments close to the value obtained in the first series of experiments. For example, if the initial value was found to be 8, then a series 7·4, 7·6, 7·8, 8·0, 8·2, 8·4 might be used.

Determination of the Best Chemical Type

Having found the optimum for the HLB value, it is now necessary to discover the best chemical type of emulsifier to use. Since this has to do with the greatest cohesive energy of each end of the surfactant molecule for its appropriate phase, some preliminary theoretical selections can be made on the basis of the simple rule 'like attracts like'. For example, if the oil phase is to contain a high proportion of unsaturated or highly branched molecules, then a choice of emulsifier based on oleates or 'iso' esters might be appropriate. Eventually, however, the final choice must depend upon trial-and-error. It should be remembered that best stability will be obtained with a mixed emulsifier system of the optimum HLB value.

Limitations of the HLB System

The above account of the use of the HLB system and the earlier sections on its theoretical basis give no more than an outline of the concept. Many studies on the limitations of the system and on the possibility of improving it have been made, none of which detract from its general usefulness. The reader is urged to study this concept in more depth.[12–15]

Orientation of Phases

Three factors combine to determine which phase will be continuous and which phase will be disperse in a cosmetic emulsion: the type of emulsifier system used, the volume ratio of light to heavy phase and the method of manufacture. All three factors are interrelated, but any one of them can exert a controlling influence—at least, during the initial formation of the emulsion. It is well known, however, that spontaneous changes in the orientation of phases can occur—a phenomenon known as 'phase inversion'.

The effect of the HLB value of a chosen emulsifier system has already been discussed. Clearly, the phase having the greatest interfacial surface tension tends to produce a concave surface so that, other factors allowing, it becomes the internal phase of the emulsion. If the surface tensions on both sides of the interface are equal—or nearly so—then inversion might be expected to take place readily. It has been shown that there is an HLB value at which inversion takes place most easily.[16]

Volume Ratio

Theoretical calculation shows that the maximum volume which can be occupied by uniform spherical particles is 74 per cent of the total liquid volume. Emulsions may, however, be prepared with internal phases amounting to 99 per cent of the total liquid volume.[17] This is possible because the spherical droplets can become distorted in shape. In such emulsions, the internal phase particles become increasingly angular as they are crowded together. Not surprisingly, the effect of high internal phase concentrations is to produce emulsions of greatly increased viscosity and their ability to remain stable depends primarily on the mechanical strength afforded by a highly condensed and structured interfacial surfactant film.

Method of Manufacture

Although there are exceptional cases, it is generally difficult for a phase to be dispersed in a stirred tank if it occupies more than 74 per cent of the total liquid volume. Either liquid may, however, be dispersed over a wide range of relative volumes (the ambivalent region) and for systems containing no emulsifier the choice of dispersed phase is often dependent on the manner in which dispersion is initiated. If a simple, two-layer mixture of water and oil phases is agitated it will tend to form an oil-in-water system if the agitator is sited in the water phase or a water-in-oil system if the agitator is immersed entirely in the oil phase, because the disperse phase is most likely to be the one that is drawn into the other. For the same reason, if the vessel is initially filled with one phase (prior to the addition of the second phase), this initial phase will be the continuous one.

It appears that the orientation of the emulsion is also affected by the type of agitator used and its speed. For a given stirrer speed, there exists a volume ratio (of light to heavy phase) above which the heavy phase is dispersed, and a region at lower volume ratio below which the lighter phase is dispersed. Between these limits lies the ambivalent or metastable region where either phase may be dispersed—but this shows a strong hysteresis effect. Thus if, at a constant stirrer speed, water is added to a stable water-in-oil emulsion the system will eventually invert at the lower volume ratio limit. If oil is now added to this emulsion, reinversion will not occur until the ambivalent region has been traversed and the upper limit reached. This ambivalent region can be increased by adding solutes which are partially soluble in both phases, such as surfactants.

As the stirrer speed is increased, the inversion points of all volume ratios tend to increase asymptotically to a constant value which is dependent upon the stirrer design. It has also been noted that for equal phase volumes at high stirrer speeds, the heavy phase tends to be the continuous one.

Another interesting point is that droplet size of dispersed phase varies with volume ratio and is greater when the lighter phase is dispersed. Thus, on inversion, a step change in droplet size occurs.[18]

These observations provide the background to various methods of practical emulsion manufacture.

Mechanism of Phase Inversion

Phase inversion is a spontaneous process and must therefore be accompanied by a decrease in the total energy content of the system. The power input at inversion does not appear to change, therefore the emulsion must be examined for a change of energy from within the system itself. It has been seen that there may be increase or decrease in the drop size and interfacial area, hence interfacial energy may increase or decrease. It does not seem possible, therefore, that inversion is concerned with minimizing interfacial energy.

Figure 38.9 is a schematic representation of an oil-in-water to water-in oil inversion. As increasing amounts of oil phase are added, agglomeration of oil droplets proceeds, enclosing small quantities of water between them. Eventually, at the inversion point, the interfacial film at the points of contact of agglomerating droplets reorientate so as to form water droplets of unusual shape which can then float away.[11]

The main observable change at the inversion point is a sudden marked decrease in the viscosity of the system as the close-packed disperse phase droplets suddenly become the continuous phase. It seems likely, therefore, that

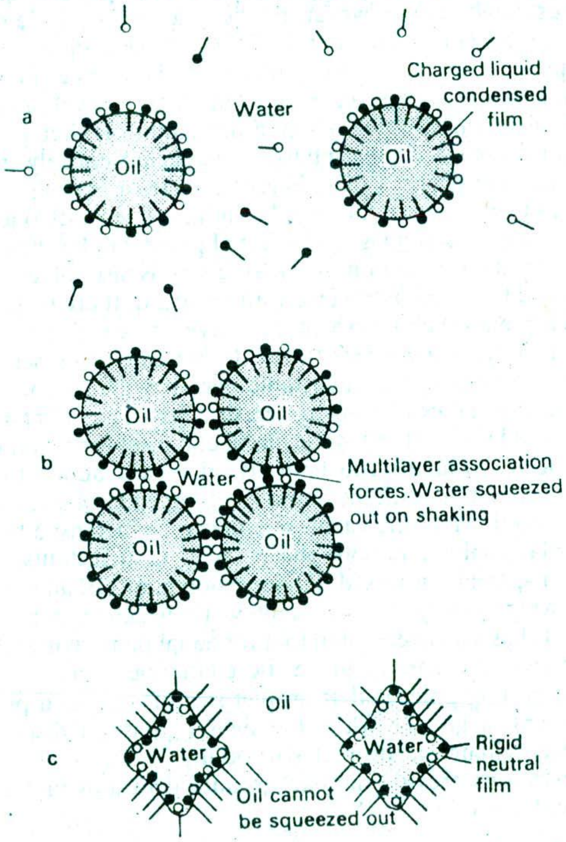


Figure 38.9 Schematic representation of phase inversion
○ Na cetyl sulphate
● Cholesterol

the energy change which brings inversion about has to do with flow and turbulent behaviour.

Except when used purposely, phase inversion is not often encountered in cosmetic production provided that the production chemist is aware of the conditions under which it can occur.[16,19] It is probably true to say that at the present time inversion cannot always be predicted but that the conditions which increase the risk can be recognized and it can be explained when it does happen.

Assessment of Emulsion Stability

Although all emulsions will eventually lose their excess energy by breaking down, it is obviously important that any commercial product should maintain its integrity throughout its useful life. In the case of cosmetic creams and lotions, the formulator has to bear in mind that they may well have to wait six to nine months on a shelf in a variety of conditions of temperature and humidity before they are purchased. The purchaser should then be able to expect these same products to withstand unfavourable storage conditions and microbiological insult for a further period of three to six months (longer in some cases) while they are in use.

The importance of the packaging in protecting the product cannot be overestimated and no emulsion should ever be placed on sale until the complete compatibility of product and pack can be assured. Even before this, however, the chemist needs information about the relative stability of his emulsion to guide him during the initial stages of formulation and pilot manufacture. Clearly, it is impossible to wait twelve months before he can arrive at a conclusion; so it is that so-called 'accelerated' storage test procedures have been devised and used in formulation laboratories. These tests take two complementary forms: those which are designed to speed up the aging process of emulsions and those designed to detect aging and measure it in an objective way.[20–25]

Because no emulsion can be separated from its environment, the influence of such factors as temperature variation, light, mechanical vibration, atmospheric oxygen and microbiological contamination cannot be ignored in any assessment of stability. For this reason, almost every cosmetic emulsion is certain to be subjected to one or more of the following accelerated aging processes at some time during its development.

(a) Storage at ambient temperature for up to nine months in glass or plastic containers.
(b) Storage at 35°–40°C for up to three months in glass or plastic containers.
(c) Storage in partially filled containers at ambient or elevated temperature.
(d) Storage at low temperatures (−5°C to +5°C) for up to three months.
(e) Storage in freeze–thaw cycle cabinets (−5°C to +30°C, two cycles per 24 hours).
(f) Centrifugation tests.
(g) Microbiological challenge tests.

It has already been pointed out that since the HLB value of a surfactant molecule is temperature-dependent, the fact that an emulsion breaks down rapidly at elevated temperature is not much of a guide to its performance at more normal temperatures over a longer period of time. Such accelerated test procedures should therefore be looked upon only as an assessment of resistance to temperature changes, and at best can only be regarded as an indication of normal ambient stability.

Centrifugation speeds up the rate of sedimentation by increasing the value of g according to Stokes's equation. Whether or not it has a measurable effect on the likelihood of cohesion once it has pushed particles close to each other is uncertain. Nevertheless, centrifugation provides a simple and rapid method of assessing the potential stability of various emulsion formulae.[26,27] Each laboratory has its own detailed methodology; a good emulsion should be able to stand up to 5000–10 000 rpm in a standard laboratory centrifuge for 30 minutes without showing signs of separation.

Increasingly, attention is being paid to those methods of emulsion assessment which give a measurement of the rate of the aging process. The oldest and probably the most widely used of these is examination by light microscopy. The size, distribution and shape of the disperse phase droplets can, to the experienced eye, tell a great deal about the emulsion and its likely stability. In particular, uneven size distribution and the aggregation of droplets are danger signs which should be looked for when comparing emulsifier performance in a given system; those giving droplets of the smaller particle size under identical conditions are obviously to be preferred.

Another approach to the monitoring of emulsion breakdown is to monitor its composite dielectric constant[25] or electrical conductivity.[28–31] In particular, the conductivity of oil-in-water emulsions can be expected to decrease with the increasing drop-size of the dispersed phase. The conductivity of a water-in-oil emulsion should be zero, but once the disperse phase particles have reached a critical size (depending on the composition of the emulsion and the applied voltage) continuous paths of conducting water phase allow a measurable current to flow. It may be said that, although not widely used, conductivity measurements have some value in the study of water-in-oil and oil-in-water emulsions.

The apparent viscosity of an emulsion depends partly upon the size distribution of the internal phase droplets. Change of viscosity is therefore another parameter by which changes likely to affect the stability of emulsions can be monitored.[32]

Generally, these storage and monitoring techniques can be valuable help in formulation, in the development of manufacturing procedures and in production control.

Characteristics of Emulsions

Having discussed the factors affecting the stability of cosmetic emulsions in some detail, it is appropriate to turn to the other characteristics by which they are judged by the user and the means by which these can be controlled.

Of prime importance when considering cosmetic emulsions is their appearance, since this can help to determine their customer appeal. Emulsions may vary tremendously in appearance from glossy opaque whiteness through a grey translucence to sparkling clarity. Opacity is due to two interrelated factors: the size of the internal phase droplets and the difference between the refractive indices of the internal and external phases. Light is reflected and refracted at each interface between droplet and continuous phase. Such changes in direction are so numerous (because of the large number of droplets) that much of the light escapes from the emulsion surface in the same direction that it entered—that is, back towards the viewer. If, however, the refractive indices of both phases are identical, or nearly so, no such reflections and refractions take place; light travels unhindered through the emulsion which has a sparkling clear appearance. This applies no matter what the size of the internal phase droplets. If the droplets are large, however, each ray of light encounters only a small number of interfaces during its passage through the emulsion. Sufficient light is reflected back towards the viewer to make the presence of the droplets obvious, but the bulk of the light, which is refracted, can find its way through. This accounts for the globular appearance of emulsions in and advanced stage of aggregation and separation. As the particle size of the internal phase diminishes, the familiar milky-whiteness appears: as the size reduction continues, the colour takes on a blueish hue, becoming grey, semitransparent and finally transparent. These changes in appearance occur as the particle size of the droplets approaches that of the wavelength of light itself. The probability that a light ray will collide with (and be reflected by) a tiny particle is enormously reduced once the particles become so small that they are comparable in size to the wavelength of light. Under these circumstances the majority of rays pass through the emulsion without being reflected or refracted and the emulsion appears to be transparent.

As the droplet size approaches that of the wavelengths at the red end of the spectrum, the reflected or refracted light is made up increasingly of smaller wavelengths at the blue end of the spectrum until, eventually, the droplets become too small for interaction at all.

In practice, it is difficult to formulate emulsions in which both phases have similar refractive indices—micro-emulsions are far more frequently found, although even these are not common (Table 38.2).

The gloss of the emulsion is a function of the microscopic smoothness of its surface. For ultimate smoothness and gloss, the internal phase particles must be relatively small and even in distribution and there must be no inclusions in the external phase such as large crystallites of stearic acid or inorganic matter of large particle size.

Table 38:2 Effect of Particle Size of Internal Phase on Emulsion Appearance

Internal phase droplet size	Emulsion appearance
⩾0·5 mm	Globules clearly visible
0·5 mm to 1 μm	Milky-white
1 μm to 0·1 μm	Blue-white
0·1 μm to 0·05 μm	Grey, semi-transparent
<0·05 μm	Translucent or transparent

Rheological Properties
The rheological behaviour of emulsions is an important subject, not only because of its influence on the 'feel' and acceptability to the consumer but also because of its impact on the manufacturing process. The science of rheology relates to matter which is being deformed or made to flow by applied forces.

Figure 38.10 represents an emulsion flowing steadily under a constant force through a pipe. The layer A in contact with the pipe is practically stationary but the central part C of the emulsion is moving relatively fast; in this sense, the emulsion is not only flowing, but is being deformed. At other layers between A and C (such as B) the emulsion has a velocity less than at C, the magnitude of the velocities being represented by the length of the arrowed lines in the figure. Since the velocities of neighbouring layers are different, a frictional force is generated between them just as in the case of two solid surfaces moving over each other.

It was Newton who first suggested that this frictional force, F, was proportional to the area of surface considered and the velocity gradient in the part of the liquid at the point of interest. Thus:

$$F = \eta A \times \text{velocity gradient}$$

where A is now an area and the proportionality constant, η, is known as the coefficient of viscosity.[33]

When materials are subjected to deformation of the type illustrated in Figure 38.10, they are often said to be under the influence of 'shearing' forces. Thus the quantity F/A is known as the 'shear stress' per unit area. To be consistent, the velocity gradient is similarly referred to as the 'rate of shear'. In this way, the viscosity of emulsions and other liquids can be defined as the shear stress divided by the rate of shear:

$$\eta = \frac{F'}{S}$$

where $F' = F/A$ and S is the velocity gradient, or rate of shear.

Evidently, for all fluids conforming to the above equation, the viscosity is independent of the rate of shear; if the emulsion is forced twice as hard through the pipe, it will flow at twice the rate. Such materials are said to exhibit

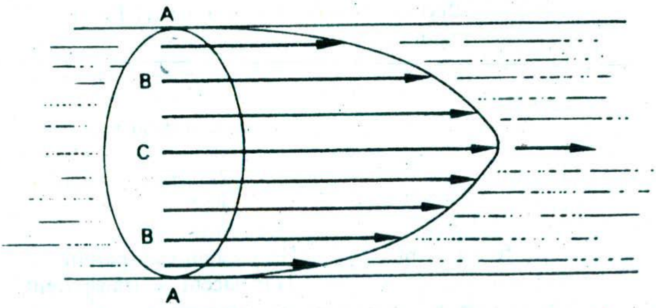


Figure 38.10 Different flow velocities of layers of emulsion in a pipe

'Newtonian' behaviour and include water, hydrocarbon oils and certain other liquids such as low-viscosity silicone oils. Many liquids, however, including the vast majority of emulsions, show deviations from this simple model and are therefore to be regarded as 'non-Newtonian'.

In Figure 38.11 curve A illustrates the relationship between viscosity and rate of shear for a Newtonian fluid; curve B illustrates the case where the viscosity apparently falls as the rate of shear increases. In some instances, a certain force must be applied before any shear (or flow) takes place at all—such materials are said to exhibit 'plastic' behaviour. Many fluids, on the other hand, merely exhibit a decrease of viscosity as rate of shear increases from zero, and these are referred to as 'pseudoplastic'. Dilatant materials 'firm up' as rate of shear increases; emulsions of this kind are infrequently encountered. Much more common are emulsions which show a degree of 'thixotropic' behaviour. Thixotropic materials exhibit reversible behaviour—in other words, after a lowered viscosity caused by increased rate of shear, a subsequent reduction of shear results in a corresponding increase in apparent viscosity. This increase may not be immediate, and recovery can be slow. The majority of emulsions are non-Newtonian and show some degree of thixotropic behaviour, although the complete recovery of the initial viscosity is not always achieved.[34]

Two factors contribute to the viscosity of emulsions: the viscosity of the external phase—which has been dealt with already—and the ratio of internal to external phase. Apparent viscosity increases with the proportion of internal phase. In extreme cases, where this exceeds 74 per cent of the total volume, the emulsion can be transformed so that it has a paste-like consistency and examination under the microscope shows that the usual spherical shape of the internal phase droplets has become angular and distorted.[17] Such viscosity is referred to as 'structural' viscosity and may be achieved with emulsions of either type.[34]

Finally, it should be noted that air trapped in the emulsion can cause a considerable increase in apparent viscosity, particularly if it is very finely divided.

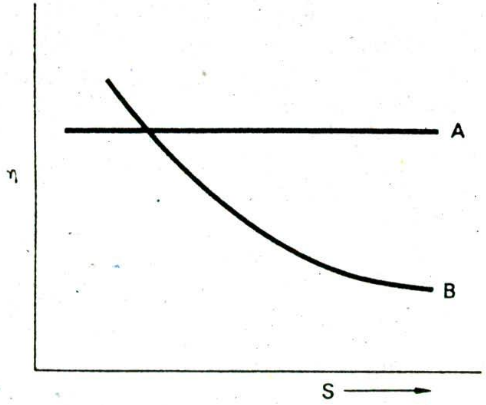


Figure 38.11 Viscosity (η) versus rate of shear (S) for a Newtonian fluid (A) and for a pseudoplastic material (B)

Application Properties

The in-use properties of cosmetic emulsions can be thought of as those which are apparent during its application to the skin or hair (the 'feel') and the after-effects once the product has been applied. Both types of property are important since even the most effective products will not appeal to the consumer if the 'feel' on initial application is unpleasant.

The initial feel of an emulsion is largely dependent on that of the external phase; thus an oil-in-water emulsion will feel like water, whatever is dispersed in the aqueous phase. Water-dispersible thickeners and additives such as glycerin, sorbitol and glycols will all exert some effect. Water-in-oil emulsions will feel oily—but whether or not they are sticky, for example, depends upon the choice of oil-phase ingredients. Viscosity also plays an important part in the initial impact of an emulsion: high viscosities tend to give a cream 'richness'.

During the application, some emulsifiers tend to promote the appearance of a foam-like whitening, often referred to as 'soaping'. Anionic emulsifiers are particularly prone to this and the effect is not always considered advantageous since it prolongs the application time.

As the water and other volatile ingredients evaporate, the 'feel' changes. Oil-in-water emulsions invert; this may happen abruptly or gradually but the difference in 'feel' as this happens, while being easy to detect, is somewhat difficult to describe in words.

Finally, the after-effects are determined by the choice of oil-phase ingredients (which may be greasy or non-greasy) and any non-volatile water-phase ingredients.

Determination of Emulsion Type

Many methods have been proposed for the determination of the identity of the external phases of emulsions. Although each has its drawbacks, a combination of all three of the following methods may be expected to give a reliable indication of the orientation of an emulsion.

(a) The emulsion is subjected to an electric voltage.[28] If no current flows, the external phase is non-conducting (that is, oily). If an appreciable current flows, the external phase is conducting (that is, water). If a small current flows, this may indicate a dual emulsion or a gradual inversion.
(b) Oil-in-water emulsions will disperse easily in water, water-in-oil emulsions will disperse easily in oil.
(c) Water-soluble dyes will spread through oil-in-water emulsions, oil-soluble dyes through water-in-oil emulsions.

Quality Control and Emulsion Analysis

The following properties of emulsions are most commonly examined for the purposes of analysis and quality control.

Colour, Odour and General Appearance.

Weight per Millilitre. Several varieties of pyknometer are commercially available for use with emulsions.

Apparent Viscosity. Several methods of determining this property are used in the cosmetics industry. Better still is the measurement of apparent viscosity at two rates of shear (preferably with a ten-fold different in shear rate) since the ratio of the two readings gives an indication of the degree of non-Newtonian behaviour (Figure 38.11).

Hydrogen Ion Concentration. The measurement of pH has been dealt with earlier in the chapter.

Water Content. Probably the best method is by Karl Fischer titration.

Volatile Content. This is usually measured by weight loss over 24 hours in an oven at 110°C.

Stability. This has already been covered.

Chemical Identity of Separated Phases. This may be required for the purposes of evaluating emulsions of unknown composition or to check that certain key ingredients (for example, preservatives) have been added to the emulsion under examination. This is a rather specialized topic and is normally reserved for the expert analytical chemist, although analysis of this type is occasionally reported in the general literature.

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Chapter Thirty-nine

The Manufacture of Cosmetics

Introduction

It is probably true to say that processing in the cosmetics industry has evolved largely through practical experience and principles gleaned by analogy with other industries rather than by many fundamental studies. While the literature abounds with reports from workers in the areas of product development and efficacy, little seems to have been reported on new production technology over the last few decades. This does not necessarily indicate that cosmetics manufacturers see no need for improving their production facilities; on the contrary, production problems—especially those associated with relatively large-scale processes—continue to cause difficulties and delays even in the largest and best equipped factories.

The greatest single obstacle to process improvement in most plants is the enormous variety of product types, each with its own set of physical and chemical characteristics, which must be dealt with during the course of a year. The need for flexibility is usually of great importance and this leads towards compromise and, except in the largest manufacturing units, away from equipment especially designed to perform specific tasks.

It is particularly important, therefore, that chemical engineers and production chemists in the cosmetics industry should understand the basic principles and characteristics of the plant at their disposal and that they should be vigilant in the search for new equipment which will perform with even greater efficiency the tasks for which they are responsible.

While cosmetics manufacture is concerned with a very broad range of processes, there are enough common elements to allow a relatively simple overall view of the subject; this helps considerably in a study of the basic principles of cosmetic production technology.

The first step in this simplification procedure is the division of the subject into two parts: bulk manufacture and unit manufacture.

Manufacture of Bulk Product

The whole subject of bulk cosmetics manufacture can be satisfactorily described with reference to three types of process: mixing, pumping and filtering (the process of heat transfer, as will be seen, can be legitimately regarded as a mixing process). Of these processes, by far the most important is mixing.

Table 39.1 represents a convenient way of classifying the mixing processes most commonly found within the cosmetics industry. Every single cosmetics manufacturing process contains at least one mixing operation and often more than one type is involved. For example, the manufacture of a pigmented

Table 39.1 Scope of Mixing Operations within the Cosmetics Industry

Type of mixing	Examples
1. Solid/Solid	
(a) Segregating	None
(b) Cohesive	Face powders, eye shadows and all dry mixing
2. Solid/Liquid	(i) Dissolution (of water-soluble dyes, preservatives, powder surfactants, etc.) (ii) Suspensions and dispersions (pigments in castor oil and in other liquids)
3. Liquid/Liquid	
(a) Miscible	(i) Chemical reactions (formation of soaps from acid and base) (ii) pH control (iii) Blending (spirituous preparations, clear lip gloss products)
(b) Immiscible	(i) Extraction (none) (ii) Dispersion (emulsions)
4. Gas/Liquid	(i) Absorption (none) (ii) Dispersion (aeration and de-aeration)
5. Distributive	
(a) Fluid motion	Heat transfer (during emulsion and other manufacture)
(b) Limited flow	Pumping (pastes and other highly viscous products)

emulsion-based foundation cream may include:

(i) Preliminary dry blending of pigments and excipient (type 1b).
(ii) Dissolution of oil-soluble and water-soluble materials separately in their appropriate phase (type 2 example i and type 3a).
(iii) Dispersion or suspension of pigments in the oil or water phase (type 2, example ii).
(iv) Mixing of the two phases to form an emulsion, possibly with the formation *in situ* of a soap as part of the emulsifier (types 3a and 3b).
(v) Adjustment of pH (type 3a).
(vi) De-aeration of the bulk (type 4).
(vii) Cooling to ambient temperature and pumping into a storage vessel (type 5a).

Not only are all these operations different from each other, but at each stage the characteristics of the bulk are quite different and require a different set of processing characteristics to achieve the optimum economic process. Not surprisingly, therefore, the optimum is rarely achieved.

The subject of pumping is not clearly separated from that of mixing since pumping implies the forced flow of product. Any flow will naturally introduce an element of mixing if the product is not already homogeneous. Further, since flow is a common element of both processes, the same product characteristics (for example, rheological behaviour) must be taken into account.

Filtering is not usually a unit operation of major importance in cosmetics manufacture except in the production of spirituous preparations (colognes, aftershave and perfumes). It is possible to regard filtering as un-mixing and certainly the flow characteristics of the filtered product are again of prime importance. The use of sub-micrometre filters for the sterilization of water is discussed elewhere in the book.

Unit Manufacture

Most cosmetic products are filled from bulk in machines specifically designed to handle the units of a particular product type. While it is true that great care must be taken in the choice and the setting up of such machines, the main problems encountered are often concerned with the characteristics of the machines themselves rather than with the manufacture or processing of the product. There are at least two areas, however, where special understanding of the product units and their characteristics are essential for the achievement of efficient production: these are the moulding processes (lipsticks, wax-based sticks, alcohol–stearate gels) and compression processes (compressed eyeshadow, blushers and face powders).

A description of unit manufacture could include all filling and packaging operations; for the purposes of this chapter, however, discussion will be confined to bulk manufacture.

MIXING—AND THE MANUFACTURE OF BULK COSMETIC PRODUCTS

Definition of Terms

The object of a mixing operation is to reduce the inhomogeneities in the material being mixed. As Table 39.1 shows, inhomogeneity may be of physical or chemical identity or of heat. Further, in the processes demanded by cosmetic manufacture, the mixing is designed to be permanent—or as permanent as it is possible to make it—as distinct from those operations (such as extraction and stripping) which rely on eventual un-mixing in order to achieve the desired objective.

Clearly, the degree to which inhomogeneity can be reduced depends on the efficiency of the mixing apparatus used and also on the physical characteristics of the materials constituting the mixture. For miscible liquids, homogeneity can be produced at a molecular level whereas for mixture of powders homogeneity is limited to the sizes of the powder particles themselves. When examing a mixture for quality, therefore, the *scale of scrutiny*—the magnification at which the mixture is examined—must vary from product to product. At an acceptable scale of scrutiny, *perfect mixing* implies that all samples removed from the mixture will have exactly the same composition. This is rarely achievable. *Random mixing* is achieved if the probability of finding a particle of a given component in a sample is the same as the proportion of that component in the whole mixture. Random mixing is the aim of all industrial mixing operations and whereas samples removed from such a mixture will not be identical, the variations should be very small. If the scale of scrutiny is reduced sufficiently, however, this may no longer be true.

Mixing can only occur by relative movement between the particles of the constituent components of the mixture. Three basic mechanisms for achieving this relative movement have been identified: bulk flow, convective mixing and diffusive mixing. *Bulk flow* (which includes shear mixing, cutting, folding and tumbling) occurs in pastes and solids, when relatively large volumes of mixture are first separated and then redistributed to another part of the mixing vessel. *Convective mixing* involves the establishment of circulation patterns within the mixture. Finally, *diffusive mixing* occurs by particle collisions and deviation from a straight line. In miscible liquids of sufficiently low viscosity, the thermal energy which is possessed by the constituent molecules may be enough to achieve a good mixture quality by thermal diffusion without additional energy being applied, although this process is usually too slow for industrial purposes.

It is incorrect to assume, however, that the relative movement between mixture particles brought about by these mechanisms always results in an improved mixture quality; on the contrary, many mixing problems arise from the tendency of mixture particles to segregate during attempts to mix them. *Segregation* is defined as the preference of the particles of one component to be in one or more places in a mixer rather than in other places. The size of the non-uniformities in an imperfect mixture is sometimes referred to as the 'scale of segregation' and the difference in composition between neighbouring lumps or volumes is the 'intensity of segregation'. Segregation is not, fortunately, a major problem in cosmetics manufacture although it does manifest itself occasionally (as, for example, in the flotation of pigments during lipstick processing).

SOLID–SOLID MIXING

Table 39.1 distinguishes between two types of solid–solid mixing operation: those concerned with segregating powders and those with non-segregating or cohesive powders. The essential difference between these two categories relates to the properties of the powders themselves and, in particular, to the freedom which individual particles have to move independently of their neighbours. Free-flowing powders exhibit many process advantages (such as easy storage, easy flow from hoppers, smooth flow of product), but have the disadvantage that they tend to segregate unless all the constituent particles are of very similar shape and size. Cohesive powder, on the other hand, lacks mobility, and individual particles are bonded together and move as clumps or aggregates. Although segregation does not appear to be a problem (except, as will be seen, at very small scales of scrutiny), cohesive powders are difficult to store and do not easily flow from hoppers.

In a powder mass, there are forces at work which tend to make the particles bond to each other and these are balanced by the gravitational masses of the particles which cause them to fall apart again. Although the bonding forces, for a given powder, are largely independent of particle size, their gravitational mass is obviously not. For this reason, particles will stick together only when they are small enough for the gravitational forces acting on them to be much smaller than the bonding forces. Powders composed primarily of such particles exhibit cohesive characteristics and those consisting of larger particles tend to be free-flowing. To a first approximation, therefore, the division between the two types of powder is one of size and the critical size is approximately 50 μm: below this particle size, powders are cohesive.

Figure 39.1 shows the particle size range of commercial grades of some powders commonly used in cosmetics production; by inference it will be noted that they are all predominantly cohesive in nature.

Nature of Inter-particle Bonds

The nature of the bonding forces between powder particles is of fundamental importance to many industries and these are now well-understood.[1–4] The characteristics which it is essential for the cosmetics production chemist to understand, however, are as follows:

1. These forces operate over very short distances. The particles must be brought into very close contact to obtain maximum agglomerate strength (as in pressing).
2. These forces are greatly enhanced by the presence of any liquid—particularly if it is easily capable of wetting and spreading over the particle surfaces.

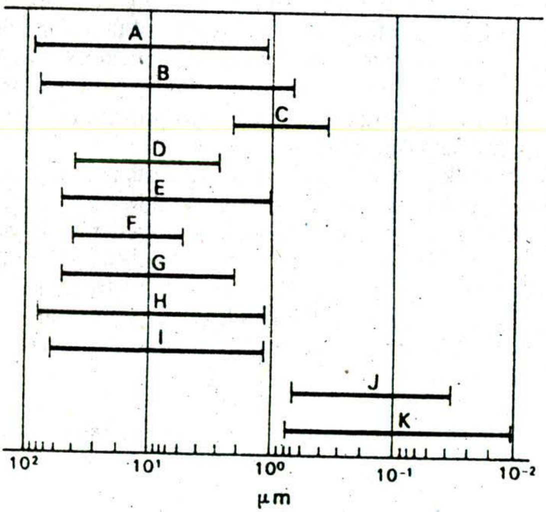


Figure 39.1 Range of particle size of some powders commonly used in cosmetics
A Titanium dioxide
B,C Magnesium carbonates
D Mica
E Zinc stearate
F,G,H Micas coated with titanium oxide
I Talc
J Organic pigments
K Inorganic pigments

3. The forces are very much weaker than those holding the particles themselves together; that is, it is much easier to break up agglomerates than it is to break up a primary particle.
4. The probability of a small particle bonding to a larger one is much greater than that of a particle bonding to another of the same size.

Manufacture of Pigmented Powder Products

Powder eyeshadows, face powders and powder blushers are commonly composed of the following types of material:

Talc
Pigments
Pearl agents
Liquid binder
Preservative

The order in which these ingredients are mixed and the process by which the mixing is carried out depend largely upon the type of equipment that is available. A satisfactory powder product, when examined under high magnification, is seen to consist of small agglomerates or single particles of the pigments adhering to and covering the surface of the larger talc particles. Improperly processed powders contain larger agglomerates of pigments existing as discrete entities and separate from any talc particles. When rubbed, for example between finger and skin surface, such improperly processed powders change hue as these agglomerates are broken and the smaller pigment groups so released follow their natural tendency to coat the larger particles. This process is often referred to as the 'extension' of pigments onto talc.

The processing of bulk pigmented powder products is dominated by the need to achieve adequate 'extension' on an industrial scale. Of all the devices which have from time to time been tried, none has proved more popular than the hammer mill (Figure 39.2). The hammer mill was designed as a comminution machine. It consists of a fast rotating shaft fitted with freely swinging hammers mounted in a cage which is equipped with a breaker plate against which the feed is disintegrated, chiefly by impact from the hammer. The very high speed at

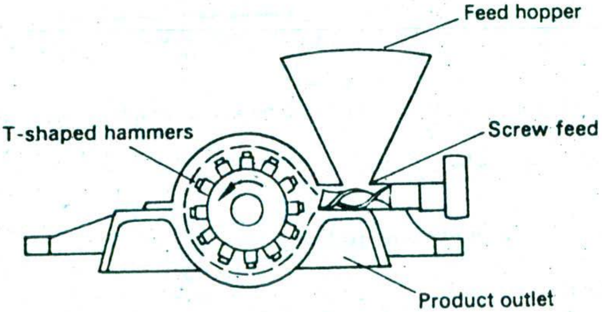


Figure 39.2 Hammer mill

which the hammers move (60–100 m s^{-1}) increases the chance of a hammer making contact with each particle and the dwell-time of particles within the chamber is increased by the placement of a variable size screen over the exit.

Hammer mills are very efficient in the comminution of brittle particles in the range of 1500–50 μm but below this size their efficiency (the probability of direct impact) falls off rapidly. This is fortunate, since it means that cosmetic talcs and micas can be passed through without being substantially altered. At the same time, however, the very high rotational speed of the hammers and the air flow within the chamber ensure that there are enough weak secondary impacts (particle–wall and particle–particle) to break the much weaker pigment agglomerates—which may be up to 50 μm in diameter. The disintegrated agglomerate fractions then stabilize by becoming coated on to larger talc particles and should not be further changed by subsequent passes through the mill.

Nevertheless the hammer mill, in its role as an extender of pigments onto talc, has certain disadvantages. For example, most of the extremely high energy which it makes available is wasted and is largely dissipated in heating the powder. From the viewpoint of energy consumption, therefore, a hammer mill used in this way is very inefficient. The feed-rate and therefore the processing time for all but the smallest batch sizes of powder is very slow. Attempts to speed up the process by the substitution of exit screens of large diameter often result in inadequate extension, necessitating a second or third pass through the mill. On the other hand, increasing the residence time of powder within the grinding chamber by decreasing this mesh size can cause the screen to become blocked with compacted powder, resulting in overheating and damage to machine and product. Perhaps the biggest disadvantage of all, however, is that the hammer mill is a continuous processing device being used for batch processing. For this reason, it must be fed with a powder mixture which has already been effectively mixed, otherwise the colour of the milled product changes as each section of unmixed bulk passes through. This preliminary mixing must be efficient although it is not necessary for any extension to be achieved at this stage.

Since the pre-mix is an additional operation and adds to the processing time, the mixer which is selected must be as efficient as possible. Probably the most widely used is the 'ribbon blender' which comprises a horizontal drum containing a rotating axial shaft which carries ribbon-like paddles. In such a device, the pre-mix can take anything between 20 and 60 minutes. Other mixers are now available which utilize higher energy input but are quicker. Table 39.2 summarizes the properties of some of the more conventional powder mixers. Since it is relatively easy to achieve good mixture quality (at a large scale of scrutiny) in cohesive powders, any mixing device will eventually produce a satisfactory even distribution of components provided that it contains no dead spots where mixing does not take place.

It is usual to add the liquid binder during this preliminary mixing stage. The binder may be poured into a suitable orifice in the mixer although many production chemists prefer to spray it into the mixer cavity as an aerosol through a venturi or similar device. This procedure helps to distribute the liquid more evenly and avoids the formation of wet, lumpy areas in the powder body. The

Table 39.2 Conventional Powder Mixers

Type of mixer	Batch/ continuous	Main mixing mechanism	Speed of mixing	Ease of cleaning	Energy consumption	Quality of extension
Horizontal drum	B	Diffusive	Poor	Good	Low	Poor
Löedige-type	B	Convective	Good	Fair	Medium	Fair
Ribbon blender	B or C	Convective	Poor	Fair	Low	Poor
Nauta mixer	B	Convective	Good	Poor	Low	Poor
V-mixer (with cutters)	B	Diffusive	Poor	Good	Medium	Unknown
Airmix	B	Convective	Good	Fair	Low	Unknown

separation of large agglomerates which takes place subsequently in the mill normally assures the completion of the wetting process provided only that the binder is correctly chosen. Should the binder still appear to be unevenly distributed after the passage of the powder through the mill, the product can often be rescued by passing it through as fine a mesh sieve as possible.

Pearl agents, especially the titanium-coated micas, present a special problem. Many of these brittle materials, which depend on their size to achieve the desired effect, are prone to disintegration in the hammer mill. For this reason, they usually have to be mixed into the bulk after its passage through the mill, necessitating an additional mixing operation. The pearl may be added in to the bulk in the same device used to perform the preliminary coarse mixing and it may sometimes be necessary to pass the bulk finally through a sieve to break up agglomerates of pearl and to ensure its even distribution.

Batch Colour Correction

It is not unusual for the bulk powder product, even though it has been correctly processed, to require colour correction in order to obtain a satisfactory match to the standard. Since any addition of pigment or talc needs to be extended, a passage through the mill is necessary. A common procedure is as follows. After the preliminary coarse mix has been completed, a small amount of the bulk (usually about 5 kg), which is assumed to be representative of the whole, is passed through the mill. This is examined in the laboratory, and if necessary, a pigment addition specified. This correction is added to the 5 kg of milled product, mixed in roughly by hand and the 5 kg is re-milled. The twice-milled sample is returned to the remainder of the bulk and re-mixed in the original mixer. A further 5 kg is then removed and the process is repeated until a match is obtained.

There is a number of minor variations to this procedure which are adopted to suit individual companies; the most important of these is the use of pigments previously extended on talc and stored as such. This has the merit of speeding up the correction process.

When pearl agents are part of the formulation, unless an un-pearlized standard is provided, the pearl must be added in the correct proportion to the laboratory sample before colour can be assessed. Pearl is only added to the bulk in the last stage of the manufacturing procedure.

Alternatives to the Hammer Mill

The drawbacks to the hammer mill as used for powder extension have led to a search for other machines which can fulfil this function more satisfactorily. The ideal equipment would probably have the following properties:

(i) It would be capable of breaking up weak particles in the size range 50–0·5 μm without damaging talc or mica particles of similar diameter.

(ii) It would be a low energy device, consuming little power itself without heating the powder mixture excessively.

(iii) It would be a batch processing device capable of mixing and extending in one operation.

(iv) It would be rapid: processing times of less than 10 minutes would be acceptable.

(v) It would not cause excessive aeration of the powder (since this causes further processing problems in later processing).
(vi) It would be easy to clean.
(vii) Its efficiency would not vary with the cohesiveness of the powder; it would not be affected by poor flow characteristics.
(viii) It would be quiet and clean in operation.

Other comminution devices have been shown to produce extension, particularly pin mills and fluid energy mills, yet none seems to work as efficiently as the hammer mill. In recent years, however, the development of high-speed powder mixers which are also capable of producing some degree of extension has brought the industry closer to the ideal. Two types in particular are worthy of mention. The first of these is best described as the vertical vortex mixer. The powder mixture is placed in a vertical, cylindrical chamber and is then accelerated outwards and upwards into a fluidized vortex motion. The motion may be produced by compressed air blasted sequentially from a series of nozzles contained in a lower cone-shaped section; alternatively, a propeller-shaped tool of 'poor aerodynamic' design may be used which rotates rapidly in the dished base of the mixing bowl. Mixing and dispersion occur at the point of conversion of the powder particles (in the upper point of the mixing bowl) by particle–particle collisions. The second type of high-speed mixer is often referred to as a 'plough–shear' device, because of the unusual shape of the mixing paddles which rotate on an axial shaft in a cylindrical horizontal mixing chamber. These paddles cause the powder from all parts of the chamber to be thrown about in such a way that it all passes rapidly through a zone occupied by a series of rapidly revolving blades on a separate shaft, referred to as a 'chopper'. The chopper is largely responsible for the powder extension and may be switched on or off independently of the main axial drive.

Both types of mixer have been used as partial or complete replacement for the traditional blender–hammer mill combination. The plough–shear type may also be used for wet-processing.

Storage of Cosmetic Powders

Two factors have an important effect on stored cosmetic powders: moisture and pressure. It is not always appreciated that a small increase in relative humidity can give rise to sufficient moisture in the stored powder to change the main mechanism of particle–particle bonding, increasing the bond strength of agglomerates by a factor of 2 or more. Such an increase in cohesiveness can make the handling and flow problems already inherent in cosmetic powders perceptibly worse and can change the processing characteristics of (say) an eyeshadow to the point where all the pressing machine settings may have to be altered to compensate.

In the same way, powder bulk that has been stored in large vertical containers exhibits increasingly difficult flow characteristics as the container gradually empties. The lower layers, having been compressed by the weight of powder above them, become increasingly cohesive as the bottom is approached. For this reason it is far better to store powder in a large number of small well-sealed containers than in loosely covered large bins.

MIXING PROCESSES INVOLVING FLUIDS

Apart from the 'dry' powder processing already discussed, the remaining processes listed in Table 39.1 involve liquids present in sufficiently large quantities as to impose fluid characteristics on the mixture. Although there are similarities between the flow of powders and the flow of liquids it is obviously easier to set up and sustain flow patterns in the latter. On the whole this makes the mixing processes easier to perform and a much larger variety of equipment is consequently available to choose from.

Even for liquids, however, the science of mixing has not yet been sufficiently developed to enable the optimum mixer to be designed for a given task from purely theoretical calculations. Much of the knowledge we have is empirical, and has been accumulated from trial-and-error practical experience; we have little detailed knowledge of many of the mixing processes at work.

General Principles of Fluid Mixing

Not only is there a great variation in the physical form and properties of substances which the cosmetics industry needs to mix, but there is also a divergence of purpose. Some mixing operations can be thought of as simple blending—for example the blending of colour solutions into miscible bulk liquids and the blending of oils, alcohol and water in perfumes and colognes. On the other hand, the formation of an emulsion, the suspending of a gelling agent and the distribution of pigment agglomerates in a viscous liquid all involve the breaking up of one of the constituents of the mixture into finer particles during the mixing process. For this reason, it is referred to as 'dispersive' mixing to distinguish it from simple blending.

On the industrial scale, mixing occurs as the result of forced bulk flow within the mixing vessel. Two types of flow can be distinguished, laminar and turbulent. Laminar flow occurs when the fluid particles move along streamlines parallel to the direction of flow. The only mode of mass transfer is by molecular diffusion between adjacent layers of fluid (Brownian motion). In turbulent flow, the fluid elements move not only in the parallel paths but also on erratic and random paths, thus producing eddies which transfer matter from one layer to another. For this reason, turbulent mixing is rapid compared with other mixing mechanisms.

When a quiescent liquid is slowly stirred the flow is laminar but as the velocity increases it may become turbulent; thus the velocity is a significant factor in determining the type of flow set up in the mixing vessel. A valuable aid in describing the critical point at which laminar flow becomes turbulent is due to Reynolds who, in 1883, first demonstrated turbulence. The dimensionless number which bears his name, Re, can be calculated for agitated vessels as follows:

$$\mathrm{Re} = \frac{D^2 N \rho}{\eta} \qquad (1)$$

where D is the diameter of the impeller, N the impeller speed (rpm), ρ the density of the mixture and η its viscosity.

Although little is known about the mechanism of turbulence, experience has shown that in agitated tanks the onset of turbulence occurs at Reynolds numbers of about 2×10^3. For fully developed turbulence, Reynolds numbers greater than 10^4 are required and are found in many cosmetic mixing processes. It can easily be seen that it becomes more difficult to achieve turbulence as the viscosity increases. Below 10–100 poise, turbulent flow can be achieved without need for an excessive amount of power—and this viscosity range covers many cosmetic products. For highly viscous pastes, however, mixing raises certain problems since the flow pattern in the mixer is invariably laminar. Under these circumstances, distributive mixing (cutting and folding) is more applicable than turbulent mixing. Turbulence not only provides rapid mixing, but also influences dispersion: it is important to understand why.

It has been pointed out in Chapter 38 that when liquids flow there is a simple relationship between the force causing the movement, F, and the velocity gradient between the layers of liquid moving at the point of measurement and the stationary or slower moving layers adjacent to them:

$$F = \eta A \times \text{velocity gradient} \qquad (2)$$

where A is the cross-sectional area of the mass of liquid under investigation and η is the proportionality constant, called the coefficient of viscosity. F/A is commonly referred to as the 'shear stress' and the velocity gradient as the 'rate of shear'. If the equation is to be believed, as the velocity of flow increases, so does the shear stress and this is the force which breaks up the weak bonds holding together pigment aggregates, or another immiscible phase into droplets. Of course, shear forces are also produced when liquids flow under laminar conditions, but under these circumstances the energy used to generate flow is dissipated largely as heat.

During turbulent flow, the energy is dissipated in disorder; eddies are produced in size and intensity depending upon the viscosity of liquid and upon F. Size reduction can only occur effectively if the eddy is smaller than the drop or aggregate. It follows that, for a liquid of given viscosity, the drop size of an emulsion or the fragmented size of dispersed pigment agglomerates depends primarily on the energy input from the agitator, the velocity gradient and the nature of the forces holding together the disintegrating entities.

Unfortunately, the simple model shown in equation (2) has limited application in cosmetics manufacture. The majority of products exhibit non-ideal (non-Newtonian) behaviour which can often be more appropriately described by the expression

$$F = (\eta_{\text{app}})^n A \times \text{velocity gradient} \qquad (3)$$

In this case η_{app} is termed the 'apparent viscosity' and n usually has a value between 0 and 1. The name given to this type of behaviour is 'pseudoplastic' and the basic difference between materials exhibiting this property and ideal or 'Newtonian' fluids is illustrated in Figure 39.3. As can be seen, pseudoplasticity is manifested by a fall in viscosity with increasing shear rate at constant temperature. Many cosmetic liquids exhibit this behaviour—especially emulsions and suspensions of particles of the order of 1 μm or less in size. Pseudoplasticity is usually reversible to some extent—in other words, when left unstirred for long enough, the fluid will recover some or most of its original

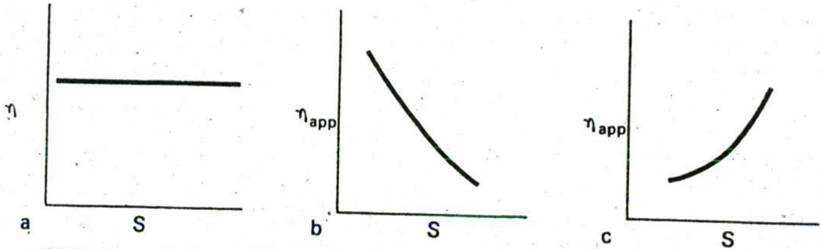


Figure 39.3 Rate of shear (S) plotted against viscosity (η) or apparent viscosity (η_{app})
a Newtonian material
b Pseudoplastic material
c Dilatant material

viscosity. The magnitude of the pseudoplastic effect is variable with the identity of the fluid, although a fall of 25 per cent in viscosity when the rate of shear is doubled is not unusual.

A related type of non-Newtonian behaviour is the property of 'elasticity'. As the name implies, elastic fluids have the ability, on being deformed by the action of shear, to recover their structure rapidly, with a consequent regain of the energy absorbed during deformation. It is probably accurate to regard elastic behaviour as an extreme of pseudoplasticity in which the recovery time is very short. Certainly it is true that all pseudoplastic fluids exhibit some degree of elasticity.

Three other types of rheological behaviour are also worth noting, although they are less frequently encountered in cosmetics processing. Truly 'plastic' fluids exhibit viscosity versus shear rate curves similar to those of pseudoplastic materials, but in this case a certain force must be applied before any shear (or flow) takes place. 'Dilatant' materials show the opposite effect, viscosity increasing with shear rate (Figure 39.3).

The term 'thixotropic' is often used erroneously to describe pseudoplastic behaviour. Thixotropic liquids exhibit a fall of viscosity with time at *constant* shear rate.

Mixing Equipment For Fluids

In the mixing of fluids, all three mixing mechanisms—bulk flow, turbulent diffusion and molecular diffusion—are usually present. As viscosity increases, however, and turbulence becomes correspondingly more difficult to establish, the parts played by turbulent and molecular diffusion become less important. Mixing equipment can therefore be divided into two categories, depending on whether or not turbulent conditions prevail, as follows:

Laminar shear/distributive mixers
Helical screw/ribbon blenders
Two-blade mixers
Kneaders
Extrusion devices
Calenders
Static mixers: low Re

Turbulent mixers
Turbine-agitated vessels
Pipes
Jet mixers
Sparged systems
High-speed shear mixers
Static mixers: high Re

Fluids with Low or Medium Viscosity

By far the most common form of mixing in liquids of low or medium viscosity is achieved by forced convection in stirred or agitated vessels. The motion of the liquid produced in the vessel must be sufficiently intense to sustain turbulence. Since it is unlikely that turbulence can be generated uniformly throughout the whole contents of the vessel on the production scale, the liquid must be circulated continuously around the vessel so that it all passes through those regions where turbulence develops. Thus the number of important basic mixing parameters to be considered is two: the extent of turbulence and the circulation rate of the contents.

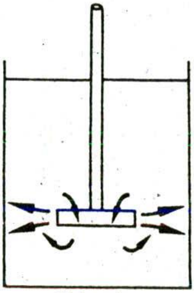
The liquid motion is very often produced by a mechanical mixer—usually a rotating impeller of some kind: two distinct types may be distinguished. In the first of these, exemplified by the rotating disc, momentum is transferred from the impeller to the liquid primarily by shear stress. As the agitator rotates, the layer of liquid immediately adjacent to it rotates with it. Viscous drag then causes the next layers to move and so on until the entire vessel contents are in motion. In order to produce efficient mixing, such systems need to be operated at high Reynolds number and develop comparatively high shear, and hence one of the main applications is in emulsification.

Far more common, however, are mixers of the second group which transmit their momentum through the pressure exerted by the impeller on the liquid (that is, in the direction of flow). Included in this group are paddles, turbines and propellers which exert pressure on the liquid in front of them as they rotate. This results in the displacement of part of the liquid in their path into the surroundings and the formation of a rotational flow pattern in the liquid. Additionally the decrease in pressure behind the blades entrains liquid from the surroundings, the effect of which is to produce turbulent eddies around the blades, especially at the blade tips. Such turbulence is, of course, extremely localized and therefore of limited value. As the impeller speed rises, however, the centrifugal force acting on the liquid increases, leading to a flow of liquid away from the periphery of the impeller, displacing and entraining other liquid and inducing further turbulence. The exchange of momentum of the flowing liquid with its surroundings results in a loss of velocity as the distance from the impeller increases, and thus the flow pattern and mixing efficiency vary according to the viscosity and flow behaviour of the fluid, the design of the impeller and vessel and the rotational speed of the impeller itself.

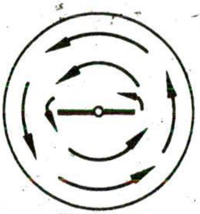
Flow Patterns. Flow patterns in agitated vessels can be resolved into three principal types: tangential, radial and axial.

In tangential flow, the liquid moves parallel to the direction of the impeller. Movement of liquid into the surroundings is small and there is little movement perpendicular to the blades except in eddies near the tips. Tangential flow may be observed in paddle mixers operating at low speeds or in liquids of sufficient viscosity to prevent centrifugal flow from being developed (Figure 39.4).

During radial flow, the liquid is discharged outwards from the impeller by centrifugal force. If the moving liquid strikes the wall of the vessel, it splits into two sections, circulating back towards the impeller where it is re-entrained. Further turbulence and mixing are induced by the splitting of the flow at the



Side view



Top view

Figure 39.4 Tangential flow

wall. There is usually some element of radial flow in agitated vessels, but flat-blade turbines produce flow patterns that are primarily radial (Figure 39.5a).

Axial flow, as the name implies, takes place parallel to the axis of rotation. Usually the impeller or propeller blades are pitched so that liquid is discharged axially—the direction of flow may be from top to bottom of the vessel or vice versa (Figure 39.5b).

Generally speaking, the most difficult flow pattern to maintain is one of axial flow.

Impellers for Liquids of Low and Medium Viscosity

Paddle mixers are simple and cheap but very inefficient for all but very low viscosity liquids. They produce mainly tangential flow and are usually mounted centrally because of their large diameter compared with that of the tank.

Turbines are probably the most common impeller type used in cosmetics processing since they can cope with a wide range of viscosities and densities. For liquids of low viscosity, the flat-blade impeller is sometimes used (Figure 39.6a and b). For very viscous materials the blades may be curved backwards in the direction opposite to the rotation, since these require a lower starting torque and seem to give better energy transfer from impeller to liquid (Figure 39.6c).

Figure 39.6d illustrates a fixed-pitch *axial flow impeller*. Used without baffles, however, the axial component generated by such turbines remains secondary to the radial flow component. Typically, impellers of this kind are used at rotational speeds of 100–2000 rpm as distinct from the low speed (15–50 rpm) of paddles.

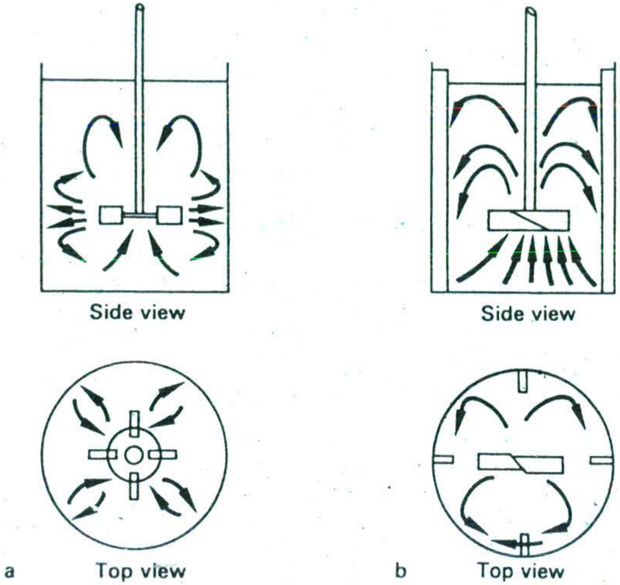


Figure 39.5 *a* Radial flow *b* Axial flow

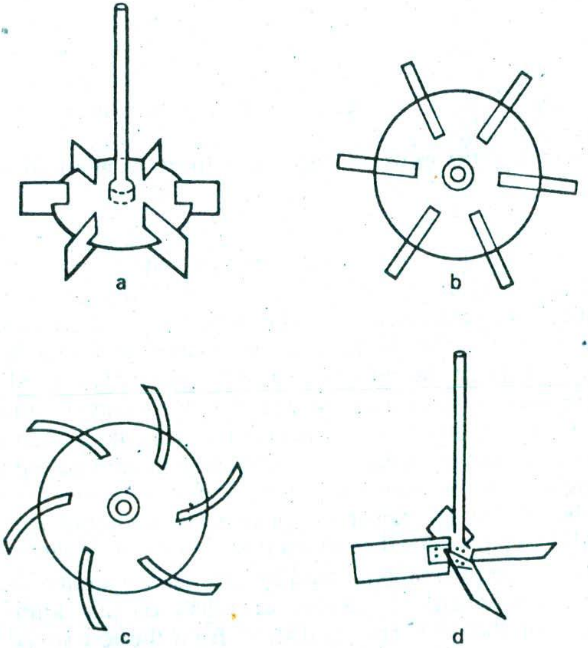


Figure 39.6 Various designs of turbine impeller

Propeller mixers are restricted to use with low viscosity fluids. They have pitched blades of which the blade angle varies along the length from centre to tip. Flow patterns developed by propeller mixers have a high axial component and the rate of circulation is high. They are usually of relatively small diameter, typically three-bladed, and are used at speeds between 450–2500 rpm. Such stirrers are used extensively in the cosmetics industry for simple blending operations but are not suitable for the suspension of particles which settle rapidly or for the dissolution of sparingly soluble heavier materials.

Many portable mixers are of the propeller type. If the mixer is mounted centrally in the mixing tank (Figure 39.7a), because of the entrainment of liquid above the impeller, the surface becomes depressed and a vortex is formed. Generally, vortices are to be avoided because of the low order of turbulence and the air-entrapment which they cause. When they are mounted eccentrically, however (Figure 39.7b), turbulence is increased and vortices avoided.

Influence of Vessel Shape

In general, the absence of smoothness and rounded corners in mixing vessels contributes to turbulence and would be expected to improve mixing times. An extreme case is the introduction of baffles around the circumference of vessels of cylindrical cross-section (Figure 39.7c). It is easy to visualize how the introduction of baffles could interfere with the flow patterns generated by tangential and radial flow impellers and cause the suppression of vortex formation in centrally mounted mixers. Experience shows that baffling improves axial flow and increases turbulence.

It will also be evident that the ratio of tank dimensions can be an important factor in determining the efficiency of any mixing process. For example, it is sensible to perform simple blending, such as alcohol–water, in tall cylindrical vessels of small cross-section using a propeller (with high axial flow). In the production of an emulsion of medium viscosity using a radial flow turbine, it would evidently be desirable to keep the height of the vessel as small as possible for a given capacity.

Mixing in Non-Newtonian Liquids of Low or Medium Viscosity

Many liquids—perhaps the majority—encountered in cosmetics processing are of the shear-thinning and/or elastic rheological type. Naturally, if the liquid is

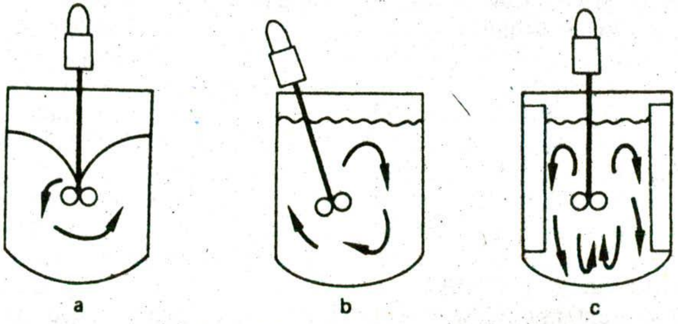


Figure 39.7 Portable mixers

already of low viscosity, the effect of shear-thinning may not be noticeable. On the other hand, more viscous liquids showing these characteristics present considerable problems to the cosmetics processor. The fluid close to the rotating impeller of a mixer is sheared at a high rate and so becomes relatively mobile, but as this is pumped away from the impeller it encounters regions of less intense flow and hence of much higher viscosity. Turbulence is therefore rapidly damped out, decreasing the turnover in the vessel and slowing down the mixing process. Moreover any elasticity shown by the liquid results in the absorption of energy by deformation of a recoverable variety, thus damping out turbulence even further.

Fluids of High Viscosity

As the viscosity of the mixture increases, it becomes increasingly difficult—and finally impossible—to produce turbulent flow within the mixer. At viscosities of 1000 poise or above, flow is inevitably laminar, power consumption high, and the rate of mixing exceedingly low. In such systems, the input power is not used to create disorder but to create heat. The rate of temperature rise is dependent upon the energy input, the thermal conductivity of the mixer and the efficiency of the cooling surfaces, but the range 1°C to 30°C per minute would include many cosmetic mixing processes of this kind. Generally it is difficult or impossible during industrial mixing of highly viscous materials to dissipate heat faster than it is generated. This is particularly true if the mixer is of large capacity (in which the ratio of volume to heat-exchange surface is high) and if appreciable films of chilled liquid are allowed to build up on the walls of the vessel, so insulating the contents from further cooling. The increase in temperature associated with such processes has both obvious advantages and disadvantages. On the one hand a rise in temperature might cause a decrease in viscosity, making mixing more efficient, and might also help in the melting or dissolution of some of the components of the mixture. Taken too far, on the other hand, the decrease in shear stress caused by the fall in viscosity can decrease the efficiency of stress-dependent processes (such as the breaking up and dispersion of pigment agglomerates), and also the rise in temperature may damage the product by causing the thermal degradation of heat-sensitive components such as preservatives and perfumes.

The relatively high energy input required to mix viscous materials also influences the mechanical construction of the mixing machinery and the method by which mixing is achieved.

Impeller Types and Mixers for High Viscosity Fluids

Propellers and turbines, as already mentioned, work best under turbulent conditions at relatively high rotational speeds. In viscous products, given that such speeds are attainable at all, flow is confined to the regions very close to the impeller, and large stagnant regions in the mixer exist where no mixing can occur without the employment of some secondary mechanism. To eliminate these stagnant regions, large impellers such as paddles, gates, anchors and leaf impellers may be used; these sweep a much greater proportion of the vessel and produce more extensive flow. Usually such impellers are designed to have close clearances with walls, giving a degree of wall-scraping. This helps to eliminate build-up of unmixed materials at walls, provides a region of high shear for dispersing aggregates and lumps, and may improve the wall heat transfer to and from the bulk.

Such impellers provide extensive flow but only of the tangential and radial variety. Axial flow—and therefore top-to-bottom mixing—is almost totally absent. For this reason, more complex designs such as the helical screw and helical ribbon have been introduced (Figure 39.8). These are more efficient for viscous mixing but their performance is poor compared with that of more conventional impellers for medium and low viscosity mixtures. Consequently, they are rarely employed in cosmetics manufacture.

Axial flow cannot be achieved by the introduction of baffles as when mixing lower viscosity fluids, but some success has been achieved by the use of impeller–draught tube combinations. As the name implies, a draught tube is a tubular, axially orientated enclosed space within the main mixing chamber containing an impeller or some other means of forcing the flow of mixture along it. Small impellers or helical screws designed to fill most of the cross-section of such a tube have been successfully used to promote axial flow in most liquids, even those of very high viscosity.

An alternative approach to the problem created by lack of flow in viscous media is the use of impellers which progressively sweep the whole contents of the vessel while the mixture remains stationary. Examples of this include the 'Nauta'-type mixer in which a helical screw sweeps the wall of a conical mixing chamber.

For even more viscous products such as mascara and very thick pastes, equipment which exhibits a greater degree of distributive mixing may be utilized. Such mixers are designed to produce bulk flow and laminar shear by spatial redistribution of elements of the mixture. Perhaps the most commonly encountered mixers of this type are of the single or double action planetary type or the two-blade 'dough' mixer. Their essential feature involves the cutting and

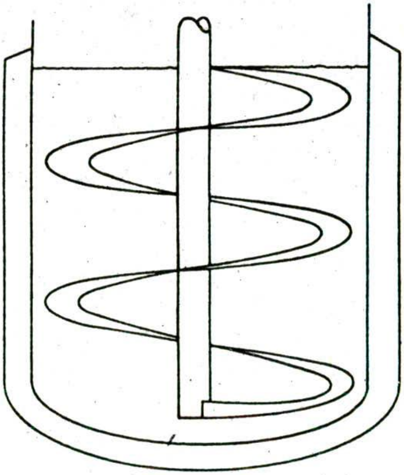


Figure 39.8 Helical impeller

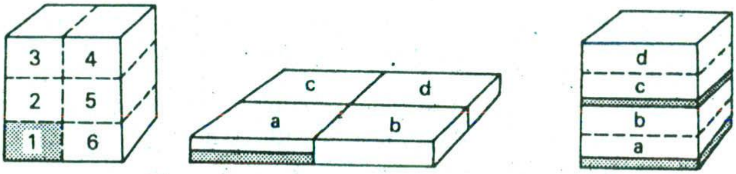


Figure 39.9 Distributive mixing mechanism

folding of a volume of the mixture and the physical replacement of it into another part of the mixer where it is cut and folded again. An example of this distributive mechanism is illustrated in Figure 39.9, in which for clarity a volume of a mixture has been isolated and divided into six equal segments, one of which consists of a black minor component.[5] The cube is compressed to one quarter of its initial height, cut and reassembled as shown. Redistribution of the minor component has been achieved which, were the process to be repeated often enough, would eventually achieve the desired level of homogeneity.

A more recent innovation is the so-called static mixer, of which several designs are now commercially available. Static mixers are essentially in-line mixing devices in which mixtures flowing through a pipe are cut and folded by a series of helical elements in a circular tube (Figure 39.10). These elements (which do not move—hence the name 'static') turn the flowing mixture through an angle of 180°. Since alternative elements have opposite pitch and are displaced 90° to each other, this causes the bulk flow to reverse direction at each junction, and thus the leading edge of each element becomes a cutting device, splitting and re-folding the mixture in on itself.

Finally, mention must be made of extruders, in which a helical screw forces the bulk mixture to flow down a tube. Here, the pressure generated can be enormous, as in soap-plodding, and such energy can cause materials with the viscosity of toilet soap to undergo laminar flow. The actual flow pattern produced is complex, being a combination of pressure and drag flow within the tube.[6]

High Shear Mixers and Dispersion Equipment

The mixing equipment which has so far been covered in this chapter is designed primarily to produce in bulk liquid mixtures flow patterns of sufficient intensity to allow mixing to take place. In the majority of cases, the pattern of shear and turbulence developed within the mixture varies according to the

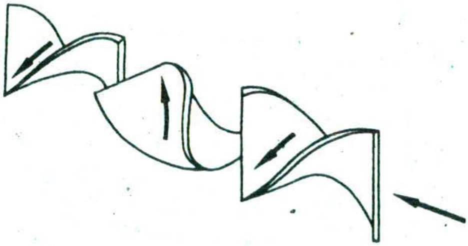


Figure 39.10 Static mixer

viscosity of the bulk, the method of producing flow and the volume within the mixture under consideration. For certain applications, however, it is desirable to generate a very intense degree of shear stress in the mixture, and for this purpose specialized equipment is available. The uses to which such machines are put in cosmetics processing include the breaking up of pigment agglomerates and their dispersion in liquids, the rapid fracture and dispersion of gelling agents (for example, bentones, cellulose derivatives and alginates) and the size reduction of internal phase droplets in emulsion products.

The basic principle on which high shear mixers work is the forcing of the mixture through a very narrow gap at the highest possible velocity. This may be illustrated with reference to a widely used device in which the mixture is entrained by a high-speed rotor, moving in very close proximity to an enveloping stator, which may or may not contain perforations through which the mixture is forced.

Figure 39.11 is a diagrammatic representation of one of the blades of the turbine separated by a very small gap, h (a few thousandths of an inch), from the stator. If the velocity of the rotor is v, then the shear rate, γ, is given by

$$\gamma = \frac{v}{h} \tag{4}$$

(γ has a typical value of 100–500 s^{-1}). It follows from the basic definition of viscosity given in equation (2) that for a Newtonian liquid having a viscosity η,

$$\eta = \frac{h\tau}{v} \tag{5}$$

or

$$\tau = \frac{\eta v}{h} \tag{6}$$

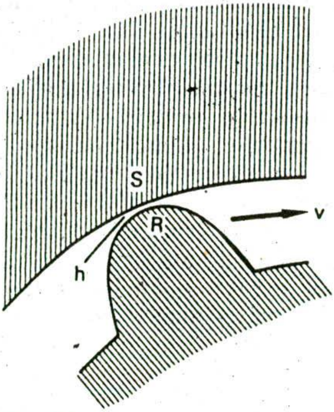


Figure 39.11 Principle of a rotor/stator high shear mixer
S = stator R = rotor

where τ is the shear stress. Thus it may be seen that shear stress required to disperse agglomerates or to reduce droplet size may be increased with increasing viscosity of the mixture, increasing velocity of the rotor and decreasing clearance between rotor and stator. For non-Newtonian liquids for which the apparent viscosity, η_{app}, is given by

$$\eta_{\text{app}} = \frac{\tau}{\gamma^n} \tag{7}$$

the corresponding shear stress is

$$\tau = \eta_{\text{app}}\left(\frac{v}{h}\right)^n \tag{8}$$

This simple treatment does not give the complete picture. Shear stress can be increased still further by the perforation of the stator, and the flow pattern over and through the shearing head may be drastically altered by the design of the assembly enclosing it. Usually, an interchangeable choice of stator designs is available with the mixer, allowing the most appropriate type to be used for a particular task. With some designs, it is possible to make use of the considerable pumping capacity afforded by the high-speed rotor.

Generally, a high shear rotor–stator mixer may be used either for batch processing in a mixing tank, or as an in-line device when it is encased in a suitable all-enveloping chamber. Used as a batch mixer, it is capable of generating considerable turbulence because of the great velocity with which fluid is pumped out of the mixing head. As with other devices, however, this high energy is increasingly converted into heat with increasing viscosity of the mixture. A serious disadvantage for certain processes is the tendency of the mixer to cause aeration when used in the top-entry mode. For this reason, such devices are often incorporated into the bottom of processing vessels.

The rotor–stator is generally more efficient when it is used as an in-line mixer, particularly as the mixing time required to ensure that every part of the mixture has passed through the mixing head is generally reduced (especially for higher viscosity mixtures). Another disadvantage is that the outer tips of the rotor may wear out rapidly, leading to increased clearance and decreased efficiency. Since no adjustment is possible, these must be replaced at considerable cost.

Another high shear rotor–stator device in common use is the colloid or stone mill. Such equipment is commonly thought of as a comminution device; this serves to illustrate the fineness of the dividing line between mixing and comminution with high shear equipment. While it is true that colloid mills may be used for the comminution of very soft materials in a slurry, they find application in the cosmetics industry for the dispersion of pigments and the size reduction of internal phase droplets in emulsions. In principle, the colloid mill consists of a rapidly rotating conical member (which may be toothed or grooved) and a similarly coned stator into which the former fits. The fluid mixture is forced through the small clearance between rotor and stator (0·5–0·05 mm) as before. Figure 39.12 illustrates the design of colloid mills in greater detail.

Colloid mills are used exclusively as an 'in-line' or continuous device. They may be water-cooled and can be adjusted as the moving parts wear down.

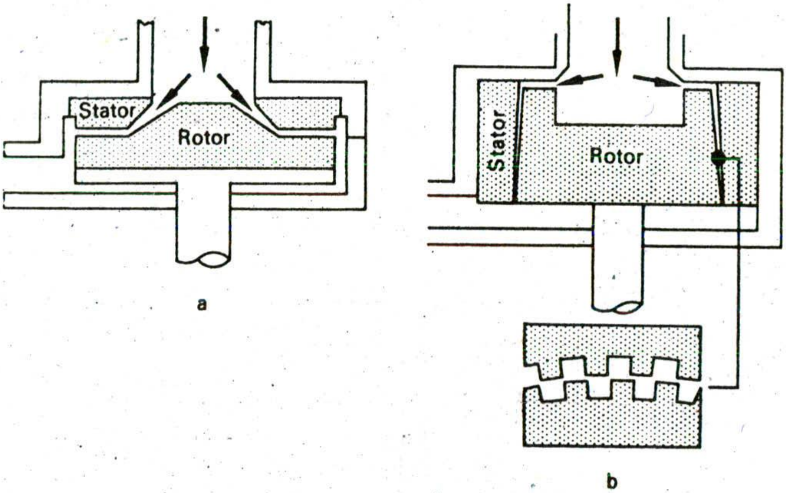


Figure 39.12 Colloid mills
a Stone *b* Toothed

For more viscous products, an alternative device is the triple roll mill (Figure 39.13). The device consists of three steel rollers which rotate in the directions indicated in the diagram. Each roller is water-cooled and machined to great accuracy so that the gaps between each pair of rollers can be set very fine. The product is applied at the top of roller A, passes between A and B and round the underside of B between rollers B and C. As it traverses each gap, the product is subjected to enormous compression forces which are particularly effective in breaking down pigment agglomerates. Strictly speaking, therefore, the triple roll mill is not a high shear device but a compression device. It is included here, however, as a real alternative to the rotor–stator mixers in bringing about effective pigment dispersion in liquids—particularly in viscous liquids.

Perhaps the highest shear stress of all is generated by a valve homogenizer, which is still extensively used in the production of emulsions with very fine internal phase droplets. A valve homogenizer (Figure 39.14) is simply a high-pressure pump which forces the product through a small orifice at pressures of up to 350 atmospheres (354 bar).

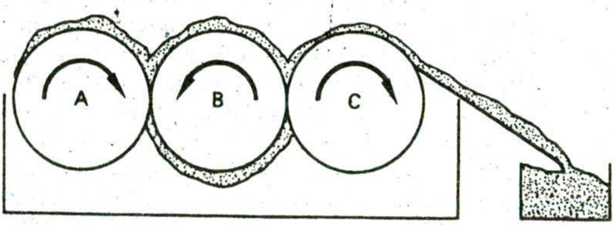


Figure 39.13 Triple roller mill

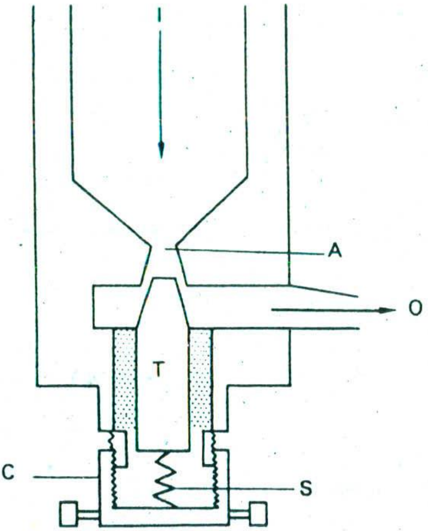


Figure 39.14 Valve homogenizer
The liquid at I is forced through the valve seating at A and leaves via O. T is a tapered shaft of which the position can be adjusted with screw head C. S is a powerful spring against which the product is pushed through the narrow valve orifice

An interesting alternative to the valve homogenizer, and one which is finding increasing use in cosmetics manufacture, is the ultrasonic homogenizer. When high intensity ultrasonic energy is applied to liquids, a phenomenon known as cavitation occurs. Cavitation is complex and not fully understood. As ultrasonic waves are propagated through the fluid, areas of compression and rarefaction are formed and cavities are produced in these rarefied areas. When the wave passes on, these cavities collapse and change to an area of compression and it has been demonstrated that the pressure in these cavities just before their collapse can be as much as several thousand atmospheres. Most of the effects of ultrasonic radiation in liquids are attributed to the powerful shock waves produced immediately following the collapse of such cavities. One design of ultrasonic homogenizer is illustrated in Figure 39.15.

No description of dispersing equipment would be complete without mention of ball mills and sand mills. In both these devices the breakdown of agglomerates is achieved by attrition between rapidly moving grinding elements which take the form of pebbles, balls or (in the case of sand-mills) finer sand-like particles < 1 mm diameter. The movement of these grinding particles may be achieved in a number of ways. In a tumbling mill, the elements tumble over each other as a horizontal drum is rotated on trunnions (Figure 39.16). Sand mills may be horizontal or vertical cylinders in which the grinding medium is stirred by a rotating agitator (Figure 39.17), whereas in vibration mills movement of the whole chamber may be caused by eccentric cams, by out-of-balance weights on a drive shaft, or electrically.

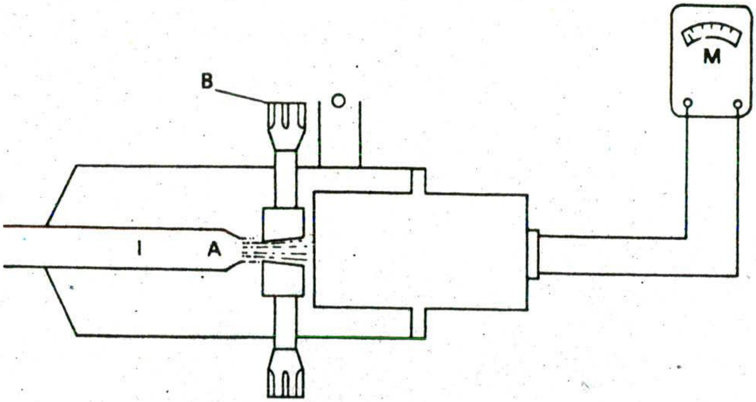


Figure 39.15 Ultrasonic homogenizer
The roughly premixed product enters at I and, on passing through orifice A, is subjected to intense ultrasonic energy by vibrating blade B. The treated product leaves via O. The meter, M, and 'tuning' devices at B combine to allow the operator to achieve maximum effect with each different product type

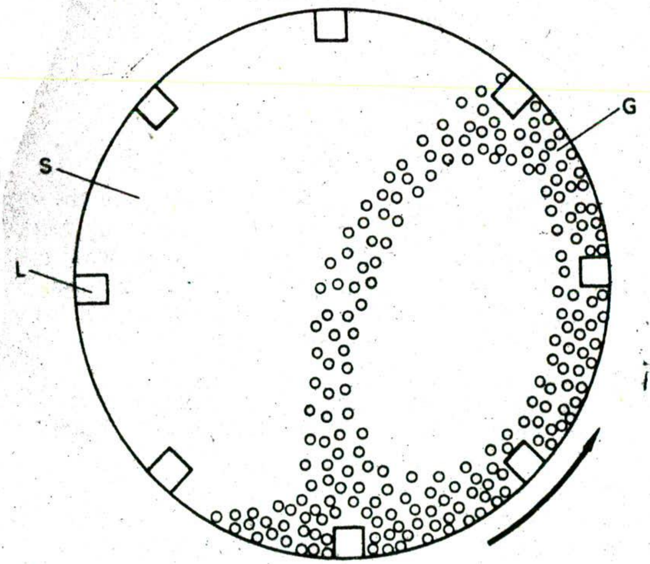


Figure 39.16 Ball mill showing ball pattern in rotating drum
G Grinding medium
L Lifter elements
S Slurry

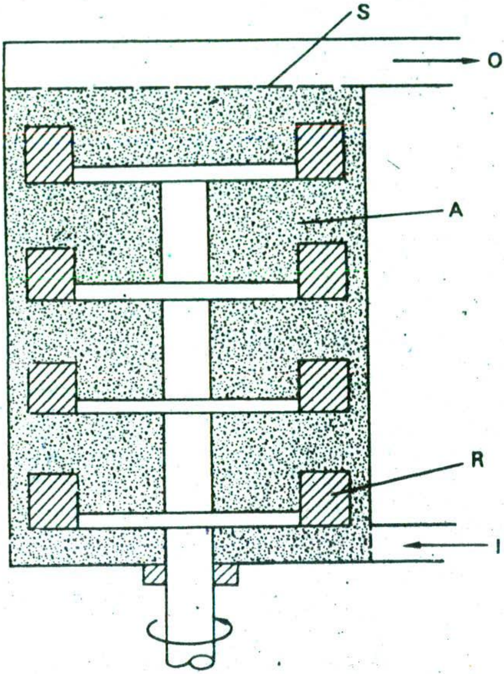


Figure 39.17 Sand mill
I Slurry in
O Slurry out
S Screen
R Rotating agitator
A Glass beads, sand or shot

Small ball mills and sand mills are used extensively in the dispersion of pigments into liquids (as, for example, in the production of castor oil lipstick pastes) and for the dispersion of bentone into nail varnish media. Although they are very effective, their chief disadvantage is the extremely protracted cleaning time required when changing from one colour to another. For this reason many users prefer to keep separate sets of grinding media for each different colour they wish to produce.

The basic mechanism by which mills of this kind produce their effect is attrition between grinding elements. Very little shear is developed.

Measurable Mixing Parameters

The science of mixing is far from complete. Designers of mixing equipment are not yet able to produce, from first principles, the optimum piece of equipment for a specific job even if they are in possession of all the parameters and fundamental characteristics of the process and mixture which they desire. One of the reasons for this is that the complete mathematical description of the flow pattern of fluid within each mixing vessel is extremely difficult and complex to achieve. Progress, however, is being made using the mathematical tool of dimensional analysis.[7–10] The serious cosmetics processing chemist is to be encouraged in pursuit of such knowledge leading, as it does, to a more thorough understanding of the equipment which may be available to him and the processes with which he must work. As an illustration, however, of the practical usefulness of the data that emerge from this analytical approach, a brief description of the relationship between some of the relevant parameters may prove useful.

Power Consumption. Power consumption is of great relevance to the economics of the mixing process. The choice of the wrong equipment can lead to the consumption of vastly greater quantities of power than are necessary to achieve the desired end result. On the other hand, sufficient power must be available and applied to the fluid to ensure that the end-point of the mixing process can be achieved in a sensible time.[8–10] Dimensional analysis requires that power input is described in the form of a dimensionless number, P_o, which is analogous to a friction factor or drag coefficient:

$$P_o = \frac{P}{D^5 N^3 \rho} \tag{9}$$

where P is the power imparted to the fluid of density ρ, and D is the diameter of the impeller which has a rotational speed of N. For many pieces of mixing equipment, P is measurable from electrical consumption data (provided that friction losses in gearboxes and bearings are ignored) and hence P_o can be calculated.

It has already been pointed out in equation (1) that another dimensionless term, the Reynolds number (Re), is useful in describing the onset of turbulence. The relationship between P_o and Re has the general form indicated in Figure 39.18. The value of graphs such as this lies in the insight they give into the interdependence of flow and mixing behaviour and the design and operating characteristics of the mixer. This should help the process engineer to choose not only the best equipment for a particular task but also the best conditions under which to operate it.

Figure 39.18, for example, shows that when flow in the mixing vessel is non-turbulent, the power which the agitator applies to the mixture falls rapidly as the agitator speed increases until, at a Reynolds number of about 200, it flattens out. If the vessel is unbaffled (curve 5), the power input then decreases again as vortex formation takes place. Here, the maximum power input that can be achieved occurs when the vortex just reaches the turbine.

The other curves show the effect of four different baffle widths. By the time the increased agitator speed has taken Re to 10^4, turbulence has fully developed. Notice that at this point the power input becomes independent of Reynolds number and dependent upon the extent of baffle. The task of the production chemist is to choose the Reynolds number and degree of baffle which will achieve the desired end result with the minimum power input.

Mixing Time. Another important measurable parameter is the mixing time, t_m. This is the time taken to achieve the desired degree of homogeneity in the mixer.

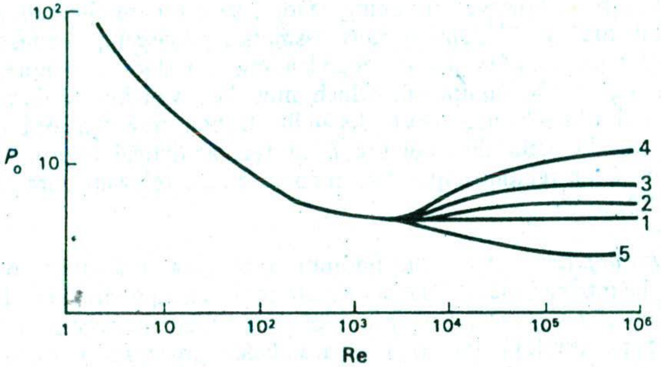


Figure 39.18 Relationship between power number, P_o, and Reynolds number, Re
1,2,3,4 represent increasing degrees of baffle
5 represents an unbaffled tank

There are many methods by which this characteristic may be measured but perhaps the most obvious is the time taken for a soluble dye to become uniformly dispersed throughout the mixing vessel (as, for example, in the manufacture of a coloured shampoo). The relationship between mixing time, t_m, and the degree of uniformity can clearly be shown if some index of mixing can be established.

A simple example of this would be the ratio of colour intensity between the top and bottom of the mixer contents at intervals after dye is added to the top (so that uniformity is achieved as the mixing index, M, approaches unity). This comparatively simple experiment should give rise to a curve similar to that shown in Figure 39.19. Since the approach of M to unity is asymptotic, t_m is difficult to measure accurately unless a colorimeter or other optical colour measuring device is available.

Once t_m has been established, however, more useful insight into the parameters controlling mixing rates may be gleaned from relationships such as that illustrated in Figure 39.20.[8,11] In Figure 39.20a (which relates to a viscous liquid in which turbulence is not established), t_m, the mixing time, has been replaced by

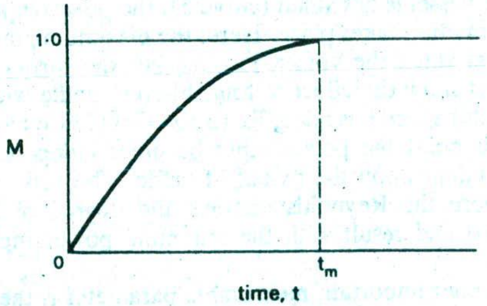


Figure 39.19 Mixing index, M, plotted against time to give mixing time, t_m

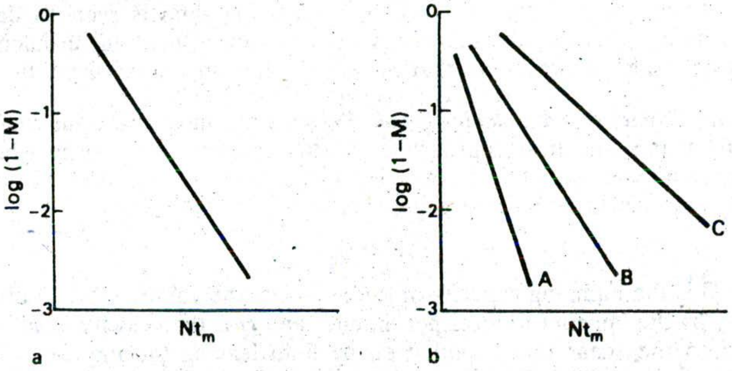


Figure 39.20 Mixing index, M, plotted against number of revolutions, Nt_m
a Newtonian fluids *b* Non-Newtonian fluids

the product of rotational speed N and t_m, that is, by the number of revolutions of the impeller.

It is interesting to note that for Newtonian fluids precisely the same plot is produced whatever the viscosity of the medium and speed of impeller. In other words, only the number of impeller revolutions determines the change in mixing index. This is not true of non-Newtonian fluids—plots A,B and C in Figure 39.20b represent liquids showing increasing divergence from Newtonian behaviour. This illustrates the difficulties, already mentioned, of mixing non-Newtonian media, in which flow is damped out rapidly by regions of high viscosity away from the vicinity of the impeller blade.

The mixing time may be converted into another dimensionless group, for example t_mND^3/v, where v = volume. The relationship between mixing time and the development of turbulence can then be elucidated. Figure 39.21 shows the general shape of curves most commonly obtained by plotting dimensionless

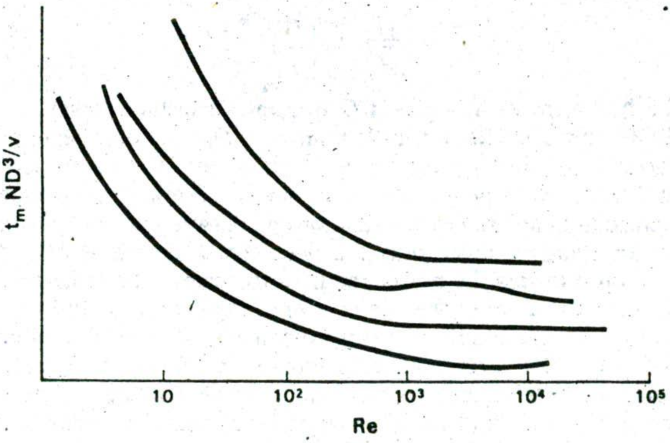


Figure 39.21 Dimensionless mixing time versus Reynolds number

mixing time against Reynolds number.[9,10] Mixing time is seen to decrease rapidly as Re increases through the laminar region. Once full turbulence has been established, however, further increase of impeller speed has little effect.

Pumping Capacity and Velocity Head. Perhaps the most powerful concept to arise from the analytical approach to mixing concerns the way in which the power provided by each type of impeller is actually transmitted to the fluid. This relationship can be expressed generally as

$$P \propto QH \tag{10}$$

where Q is the pumping capacity of the impeller (the volume of fluid displaced directly by the impeller in litres per minute) and H is the velocity head—this is related to the shear rate experienced by fluid leaving the impeller. A large slow-moving impeller might produce, for example, a large pumping capacity and a low-velocity head, while a small impeller operating at high speed might produce a lower volume of fluid pumping but at a much higher velocity head. Some cosmetics production processes—perhaps the majority—require a high pumping capacity; others require a high shear rate or velocity head. It is therefore useful to know the parameters that affect both these functions and how they interrelate.

For simple blending operations (the manufacture of shampoos or colognes, for example) pumping capacity is often of the greatest significance. Under conditions of laminar flow, the number of complete circulations of the bulk ('turnover') required to bring about homogeneity is approximately three. For a turbine operating in turbulent conditions, this is reduced to about 1·5. However, given that only a fixed amount of power is available from the motor, it is not likely that a relatively small turbine will have sufficient pumping capacity to push a fairly viscous product around by even this amount.

Not surprisingly, the factor which determines whether power is used as pumping capacity or velocity head is the ratio of impeller to tank diameter (D/T). Experiments have established the following relationship over a wide range of conditions

$$\left(\frac{Q}{H}\right)_P \propto \left(\frac{D}{T}\right)^{2\cdot66} \tag{11}$$

where the first term is the ratio of Q to H at a constant power. As shown in Figure 39.22, however, there is little point in a D/T ratio of beyond 0·6.[12] The total flow includes flow generated by entrainment of quiescent liquid in the direct flow from the impeller head and may be several times greater than Q.

The picture is completed by the relationship between power consumption and D/T ratio for equal process results in a given vessel (Figure 39.23). The use of a larger D/T ratio lowers the power required to achieve the same end result. At the same time, this implies the use of lower impeller speed and this inevitably means that the torque required to drive the mixer increases dramatically.[12] The amount of torque that a given mixer is able to accommodate depends largely on its construction. It therefore becomes a question of economics whether to invest in a more substantial (and therefore expensive) mixer in order to reduce the power consumption needed to achieve a given mixture quality.

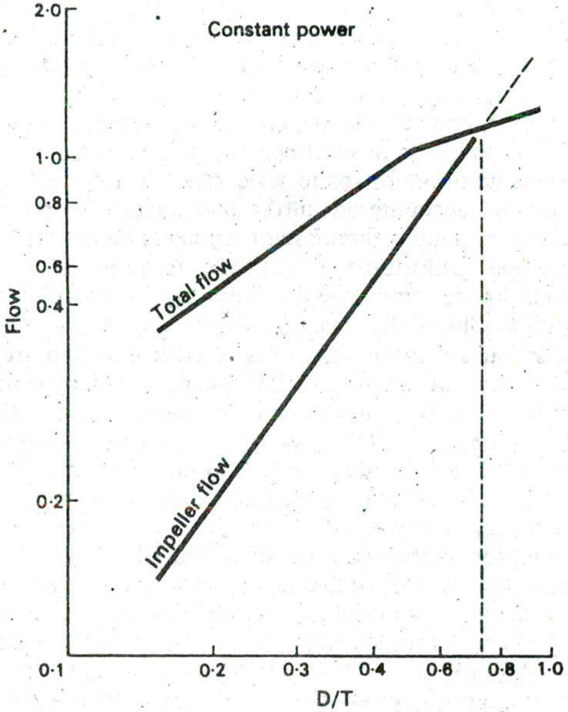


Figure 39.22 Impeller flow and total flow as functions of *D/T*

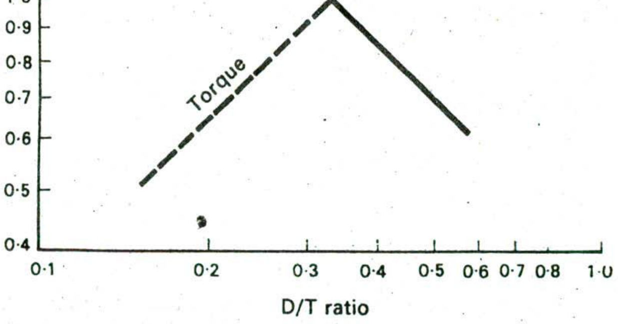


Figure 39.23 Effect of *D/T* on power consumption and torque

Scale-up

It is not unusual for a product that has been developed and made successfully in the laboratory (using laboratory stirrers and beakers) to exhibit quite different characteristics when made on a production scale. This is not due to the incompetence of the manufacturing department but represents the difference in conditions experienced by the product because of the change of scale. Even if a pilot plant is available of intermediate scale, there is no guarantee that severe problems will not be encountered during manufacture of the first full-scale batch. The study of scale-up is therefore of fundamental importance to efficient cosmetics production. Unfortunately, it is also an extremely complex subject since the variables that determine the distribution of forces within the processing vessel vary considerably as the scale changes.[12]

The quantities that are most often considered in scale-up are total power, power per unit volume of liquid, impeller speed, impeller diameter, the flow from the impeller, flow per unit volume, peripheral speed, D/T ratio and Reynolds number. For a ten-fold increase in scale in geometrically similar vessels, it is impossible to keep all of these constant. For example, if power per unit volume is held constant during scale-up from 200 litres to 2 tonnes, then every other parameter varies.

The task of the process chemist is therefore to understand which characteristics are controlling the process, so that he knows which parameters must be kept constant and which may be allowed to vary. For example, the manufacture of an emulsion requires turbulence (Reynolds number) to be held constant in order to achieve consistent droplet size of the internal phase. At the same time, the flow must be great enough to ensure that all the constituents pass through the turbulent regions.

In general, it may be said that there is not always sufficient awareness on the part of the development chemist of the problems arising from scale-up. There is no point in producing a superb new product in the laboratory which it is impossible to make in the factory. A pilot plant experiment can be a valuable tool in choosing the equipment and processes needed for full scale production but not if the study is made in a superficial way. This is an area where a fundamental understanding of mixing processes and a willingness to experiment will prove most fruitful.

SOLID–LIQUID MIXING

The production of a cosmetic product often involves the incorporation of a powdered solid material into a liquid. The objective may be to dissolve the powder completely (as with salt or preservatives in water), to effect a colloidal dispersion of water-swellable particles (as with bentones and other gelling agents) or simply the dispersion of insoluble materials such as pigments. To do this efficiently with a wide range of powder particle size and surface characteristics and with a range of different liquids of varying viscosity, quite a variety of mixing equipment is available.

Perhaps the easiest of these processes to carry out is the dissolution of a fairly large size, smooth-faced solid, such as salt. The initial incorporation of each crystal into the liquid involves the complete replacement of the air–solid surface with a liquid–solid surface. This may be considered to be a three-stage process of adhesion, immersion and spreading (Figure 39.24). Immersion is complete when all the air has been displaced and the surface of the crystal has been completely wetted by the liquid. This process is aided by a low surface tension and low contact angle between the liquid and solid.

Not all powders used in cosmetics, however, have such favourable size and surface characteristics. The majority are of extremely small particle size and, as has already been noted, highly agglomerated. Each agglomerate will have a complex structure with an uneven surface and will be perforated by cavities of irregular shape. The complete wetting of such structures, involving the penetration of liquid into all the crevices and cavities together with the expulsion of air, is very much more difficult. It should be noted, for example, that penetration into cavities requires a low contact angle but a high surface tension—in conflict with conditions for easy wetting.

Even more complex is the immersion of powders which swell in the liquid to form dispersions of colloidal size, since the particles on the outside of each agglomerated mass tend to swell and adhere to each other, slowing down penetration of the liquid to the still-dry core.

Powders that are small enough in particle size to form agglomerates are by far the most commonly used in cosmetics processing. In the dry state they entrap an enormous quantity of air (a bag of cosmetic-grade titanium dioxide, for example, contains only 25 per cent of powder together with 75 per cent of air). The majority of this air must be expelled if a smooth uniform mixture is to be obtained.

Immersion is only the first stage in the production of cosmetic quality dispersions. Even if the agglomerates were evenly distributed, the larger of them would give rise to 'grittiness'. Further, for pigments maximum colour can only be developed when these agglomerates are broken up and the maximum possible surface area of pigment is exposed. Disagglomeration is therefore the next step in the production process.

The forces holding these agglomerates together are precisely the same as those described earlier in the chapter in the section on powder mixing. The obvious difference, of course, is that these agglomerates are situated in a fluid medium, the physicochemical characteristics of which may enter into the reckoning of bond strength, ease of separation and likelihood of reagglomeration. Consequently, the theoretical treatment of particle–particle interaction in

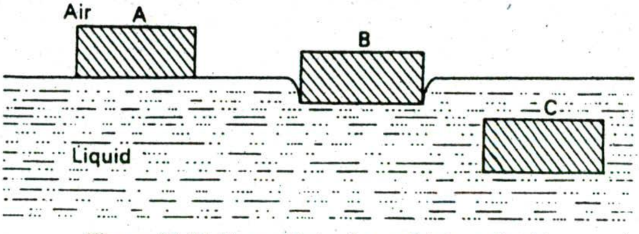


Figure 39.24 Immersion of a solid in a liquid
A Adhesion B Immersion C Spreading

liquid media is even more complex than for dry solids—although this has been extensively studied and written about.

In cosmetic processes, the disagglomeration of solid particles in liquid media can be brought about by a variety of machines. In lipstick processing, for example, pigments are 'ground into' castor oil by preparing a coarse mixture which is then passed over a triple roll mill, or further ground in a colloid mill, ball mill or sand mill. These machines are used specifically because they will deal effectively with media of lipstick-paste viscosity.

For less viscous media (for example, the dispersion of pigments into the aqueous phase of an emulsion), a high shear device of the rotor–stator type is frequently used. In this case, processing time can be shortened by ensuring that the whole contents of the vessel are brought into the catchment area of the shearing head by secondary stirring. As with all disagglomeration, shear stress is largely responsible for the partial disintegration of the agglomerate.

For soluble powders, the enormous increase in the solid–liquid interface brought about by immersion and disagglomeration will ensure that the actual process of dissolution can proceed at the maximum possible rate. For insoluble powders, however, there remains the problem of maintaining a good stable dispersion.

Disagglomeration is usually a reversible phenomenon and it can usually be assumed that the opposite process—'flocculation'—will be simultaneously taking place.

It was noted when considering powder–powder dispersion that stabilization could be achieved by the introduction of particles of larger size to which the disintegrated agglomerates could adhere. In some cases this can be applied to solid–liquid systems—for example, by pre-extending pigments onto talc before adding them to a liquid foundation base—but in many instances all the solid particles are of too small a size for this to be done. Under these circumstances rules similar to those used in emulsion technology can be applied. Thus the rate of flocculation can be slowed by some or all of the following means:

(i) The use of surface-active agents (sometimes as polymer coating of the powdered solid) to inhibit flocculation by steric hindrance.
(ii) The manipulation of electrostatic charges on the surfaces of the powder particles.
(iii) The manipulation of the viscosity of the dispersion.

Surface-active agents have a part to play at two stages in the process of manufacturing a stable dispersion. It has already been seen that the lowering of the solid–liquid contact angle speeds up the wetting process. In practice, the best results are often achieved not with a surfactant, which measurably lowers the surface tension of the liquid, but with what is sometimes described as a 'surface activator' which reduces the interfacial tension between solid and liquid. These surface activators (which are also described as 'dispersants' or 'wetting agents') can, if correctly chosen, cause an immediate improvement in the quality of the dispersion which is made manifest by a sudden increase in the colour intensity.

The rules for choosing a wetting agent or dispersant are similar to those used for surfactants in emulsions: part of the molecule must have affinity for the liquid medium and part for the solid. Clearly, if those parts of the molecule which have affinity for the liquid are large and present in sufficient numbers, by spreading out around each solid particle they can form a physical barrier that prevents particles from coming close enough together to reagglomerate. In this way an iron oxide dispersion in castor oil, for example, could be stabilized by the addition of a wetting agent having a hydrophilic end which would adhere to the oxide surface, and a long unsaturated fatty acid end which would be able to extend out into the castor oil medium surrounding each particle.

Where the liquid medium has a sufficiently high dielectric constant, other types of dispersion can be stabilized by surface activators having a residual electrostatic charge associated with them, thus preventing the flocculation of particles by the mutual repulsion of like charges.

A significant difference exists, however, between emulsions (where the two phases must perforce have very different chemical affinities) and dispersions of solids in which, for example, a hydrophilic surface can be dispersed in water. When this happens, this matching of affinities is an advantage. This has led to the processing of powders in order to coat their surfaces with a chemical (usually polymeric) of suitable characteristics to allow easy wetting and dispersion. Nowhere is this more clearly illustrated than in the case of water-wettable and oil-wettable grades of titanium dioxide. In this instance, the same grade of titanium dioxide can be coated with different resins to modify the surface in such a way as to make it wettable by either water or oil.

In aqueous media, the possibility exists for the particle surfaces to become electrostatically charged. This is an important consideration in the discussion of flocculation. For example, the effect of pH on the quality of pigment dispersions in emulsion-based products is often overlooked until it causes a problem by giving rise to an unexpected colour change. For those dispersions, particularly oxide surfaces, in which electrostatic repulsion is part of the stabilization mechanism, flocculation can occur rapidly as the isoelectric point is approached, if the pH is allowed to vary during manufacture.

Naturally, since particles have to move towards each other in order to flocculate, the viscosity of the medium through which they must move has a part to play in the rate of flocculation. It is necessary, however, to distinguish between the viscosity of the total dispersion which, as will be shown, is influenced by the solids content, and the intrinsic viscosity of the liquid medium itself; it is the latter which predominantly influences the rate of flocculation in low solids-content dispersions. The addition of thixotropic gums to nail lacquers and of colloidal thickeners to the aqueous phase of emulsions serves to slow down flocculation without materially influencing the basic flocculation process itself. For this reason the reheating of liquid pigmented foundation products sometimes results in unexpected changes of hue which are often erroneously ascribed to phase-inversion. The truth is that the rate of flocculation of an intrinsically unstable dispersion has been speeded up because of a drop in viscosity caused by the heating process.

Notwithstanding the viscosity of the liquid phase, it is generally true that the viscosity of the dispersion increases with the solids content, as does the difficulty of maintaining a good dispersion. For a given solids content, viscosity decreases with the particle size of the solid phase, and thus disagglomeration is usually accompanied by a fall in viscosity as well as a deepening of colour. In the same way, the substitution of one pigment by another with a different particle size can lead to a change of viscosity, and so it is, for example, that in order to achieve the optimum viscosity for the dispersion of pigments into castor oil, the ratio of pigment to oil may vary from one colour to another.

Suspension of Solids in Agitated Tanks

If a particulate solid is dispersed in a liquid in which it does not dissolve and the suspension so formed is allowed to stand undisturbed in a vessel, provided that the densities of the two components are dissimilar some degree of settlement or flotation will eventually take place. Where the particles are present in sufficiently low concentration to have a negligible effect on the viscosity of the suspension, re-suspension can be achieved by the establishment in the liquid of flow patterns of sufficient turbulence. The suspension of solids in agitated tanks is frequently encountered in cosmetics processing, as an aid to dissolution or as a means of obtaining a good dispersion of particles prior to a change of viscosity of the liquid medium by gelling or cooling. Although the theory concerning flow patterns in agitated tanks has already been discussed, it is necessary to reiterate that it is axial flow which is of prime importance in the movement of solid particles away from the top or bottom of a tank and that this can best be achieved with the aid of baffles. These are essential for effective particle suspension.

Three conditions can be recognized during the production of a suspension, namely complete suspension, homogeneous suspension and the formation of bottom or corner fillets.

Complete suspension[13–17] exists when all particles are in motion and no particle remains stationary on the bottom or surface for more than a short period. Under these conditions, the whole surface of the particles is presented to the fluid, thereby ensuring the maximum area for dissolution or chemical reaction. Complete suspension is achieved when the agitator has reached 'complete suspension speed' N_s. At this point there is normally a decrease in concentration of solids with tank height, with a clear liquid zone at the top. The concentration decays and clear liquid depth increases rapidly with increasing particle size and density difference. A summary of the factors contributing to the establishment of N_s and complete suspension can be obtained from the following correlation:[14]

$$N_s = \frac{S\nu^{0\cdot1}d^{0\cdot2}[(g\Delta\rho)/\rho]^{0\cdot45}X^{0\cdot13}}{L^{0\cdot85}}$$

where S = a constant
ν = viscosity
d = particle size (cm)
g = force due to gravity
$\Delta\rho$ = density difference between particle and fluid
ρ = fluid density
X = percentage w/w of solids in suspension
L = agitator diameter (m).

Homogeneous suspension exists when the particle concentration and (for a range of sizes) the size distribution are the same throughout the tank. The homogeneous suspension speed is always considerably higher than N_S and more difficult to achieve and to measure. Nevertheless, homogeneous suspension is very desirable for certain types of cosmetics applications and particularly so for continuous processing. In practice, for such processes the requirement is only that the particle size distribution and concentration in the discharge and the vessel are the same.

Sometimes heavier particles are allowed to collect in corners or on the bottom of the vessel in relatively stagnant regions to form *fillets*.[18] This may have the practical advantage of very large saving in power consumption compared with the energy that may be needed to achieve complete suspension (provided, of course, that this saving offsets the loss of active solids in the fillets).

In general, it may be said that propeller or 45°-angle turbines offer the best advantage for rapid suspension for low power consumption—particularly if draught tubes are introduced. If, on the other hand, radial flow agitators need to be used, these should be of relatively large length-to-diameter ratio, be placed close to the bottom of the tank and have turbine blades extending to the shaft to prevent problems with central stagnant regions.

LIQUID–LIQUID MIXING

As indicated by Table 39.1, it is convenient to consider separately the case in which the liquid components are all mutually soluble and the case in which some or all of them can coexist as separate phases (that is to say, they are sparingly or partly soluble in each other).

Miscible Liquids

The mixing of miscible liquids (blending) represents perhaps the simplest mixing operation in cosmetics manufacture. Several examples have already been cited and no further elaboration is needed except to reiterate that it is important to choose the mixing apparatus best suited to the viscosities of various components in order to carry out the operation efficiently.

Immiscible Liquids

Practically the only representatives of this category of mixing operation are emulsions. The theory of emulsions is covered fully in Chapter 38; briefly, all cosmetic emulsions consist of two major immiscible liquids, one dispersed as fine droplets in the other and separated by a layer of surface-active agent at each liquid–liquid boundary. (This is a simple view. In practice the two main phases are not always liquid at room temperature, and the total number of composite phases may be greater than three—this in no way invalidates a general discussion of the process available for the manufacture of emulsions.)

The Emulsification Process

The two major phases (these will be referred to as 'oil' and 'water') together with the emulsifier are brought together under turbulent conditions. Depending on the prevailing conditions, one major phase is broken up into droplets (predominantly by the action of shear stress imparted by turbulent eddies) and distributed throughout the other major ('continuous') phase.

While the droplets remain larger than the eddies, they will continue to break up into ever smaller droplets. Eventually a point is reached in this process when the available power giving rise to the turbulence cannot provide the shear stress necessary to reduce the droplet size any further. All this stage there exists an emulsion containing droplets of a certain mean diameter but over a range d_{min} to d_{max}. Provided that it is correctly chosen, the emulsifier prevents the rapid coalescence of these droplets and a stable emulsion is formed.

In order to obtain products of maximum stability that can be made consistently from batch to batch, it is desirable to keep the droplet size range as small as possible. In an agitated tank, droplet size is smallest near the impeller in the region of greatest turbulence whereas the maximum droplet size is to be found in any quiescent region of the tank. Thus it can be seen that d_{min} is fixed by the power available to generate turbulence and d_{max} depends on the efficiency of the mixing machinery fitted in the tank in producing a good circulation rate (so as to bring all the contents through the region of maximum turbulence).

Superimposed on the effect of circulation patterns in the vessel is a further factor affecting the range of particle sizes of the droplets. Theoretical considerations show that the mean droplet size is proportional to $N^{-6/5}$ (where N is the agitator speed) whereas d_{min} is proportional to $N^{-3/4}$. For a given vessel and agitator, therefore, the effect of increasing the stirrer speed should be to reduce the particle size range to a minimum after which a further increase in speed should give rise to instability and rapid coalescence (Figure 39.25). In practice, coalescence does not take place if a suitable emulsifier is present; nevertheless the graph shows the importance of attaining the correct agitator speed in reducing the particle size range to a minimum.

Orientation of Phases. In any emulsion the orientation of the phases (that is, whether the oil or the water phase is continuous) is determined principally by the choice of emulsifier and the volume ratio of oil to water. Usually, however, there is a range of volume ratio over which either phase may be dispersed, depending upon the method of manufacture. If a quiescent mixture of two phases coexisting as two simple layers (one upon the other) is agitated, the phase into which the agitator is placed is most likely to form the continuous phase in the resulting emulsion. In other words, drops are drawn into the phase in which the impeller is placed. If initially only one phase is present in the mixing vessel containing the impeller, an added second phase will inevitably form the disperse or discontinuous phase. If, however, the continued addition of the second phase combined with the choice of emulsifier eventually leads to a volume ratio at which the system is more stable with the added phase being continuous, then the emulsion will spontaneously invert to achieve this end result. When inversion takes place, it is very often accompanied by a change in droplet size. Where this

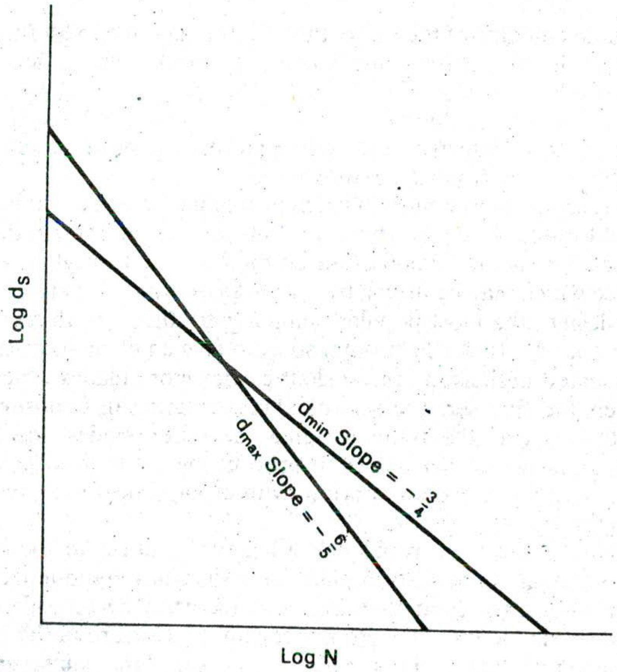


Figure 39.25 Relationship between drop size, d_s, and stirrer speed, N

change is a decrease, then inversion leads to a more stable emulsion and gives rise to a valuable method of manufacture.

Addition of Surfactant. In a batch manufacturing process for emulsions, there are four possible methods of adding the emulsifier. The first of these involves dissolving (or dispersing) the emulsifying agent in water, to which the oil is added. An oil-in-water emulsion is initially produced but inversion to water-in-oil may take place if more oil is needed.

Alternatively, the emulsifier may be added to the oil phase; the mixture may then be added directly to water to form an oil-in-water emulsion or water may be added to the mixture to form a water-in-oil emulsion. Many emulsions, on the other hand, are stabilized by soaps which are formed at the interface between the two phases. In this case, the fatty acid end of the soap is dissolved in the oil and the alkaline component is dissolved in the water. The two phases can be brought together in any order.

Finally, a less used method is one in which water and oil are added alternately to the emulsifying agent. Usually, the improvement in product quality obtained by the use of this method does not warrant the complication it causes in the manufacturing procedure.

Batch Processing Equipment. It will be evident from the discussion so far that there are at least two important elements of emulsion processing, namely shear (for the emulsification and particle size reduction process) and flow (in order to bring the whole contents of the vessel through the region of high shear). Flow is also important in the heating and cooling of the emulsion. Most emulsion processing vessels are equipped with a jacket through which steam or hot water can be circulated to heat the contents and cold water circulated to cool them. Evidently then, to be effective, the mixing mechanism must be able to provide adequate flow to and from the vessel walls.

For these reasons, most emulsion batch processing vessels contain a high shear turbine or rotor–stator device (typically bottom or side entry rather than top entry, to decrease the likelihood of air entrapment) and a high flow, low shear mixing device which may be driven by a separate motor. This high flow device is of variable design, the most popular being a gate stirrer in which the arms are inclined at about 45° to the horizontal so as to give an element of axial flow. In more complicated designs, a central shaft carries more blades which sweep the area between the first set, the sets of blades rotating in opposite directions. Whatever the design, the frame holding the outer blades normally carries spring-loaded plastic scraper blades to prevent the build-up of product on the inner vessel wall, which would interfere with efficient heat exchange across the surface (Figure 39.26).

The main motor may be driven by electricity or by air (up to about 100 psi or 9 bar). The advantages of air-driven motors are that they are infinitely variable in speed, torque-sensitive (and therefore less likely to become damaged when subjected to sudden loads), they do not constitute a hazard in the processing of low flash-point materials and generally they require less maintenance. Electric motors can be built to match some of these advantages (with slipping clutches and flameproofing), but only at considerable expense.

This traditional gate-type impeller system suffers from the grave disadvantage of limited axial flow. This is not noticeable in smaller vessels (below 600 litres capacity) but becomes a major problem in large tanks. One approach to the problem is to provide top-to-bottom transfer of the contents by means of a pump and an external pipe. A more satisfactory arrangement for the manufacture of emulsions of medium and low viscosity is to replace the gate stirrer by one or more axial flow impellers mounted centrally on a single central shaft. Although it becomes more difficult to provide wall-scrapers, the excellent flow around the vessel walls makes scraping less necessary.

The problem of ensuring that all the product passes through the region of high shear has led to the idea of passing the batch through an external circuit containing an in-line homogenizer; this may be a rotor–stator device, colloid mill or valve homogenizer.

Continuous Processing. In view of the difficulties encountered in manufacturing large batches of emulsion, a logical extension of an external circuit with in-line homogenizer is a continuous processing plant. A simple form of such a plant is illustrated diagrammatically in Figure 39.27. Such a plant is more correctly referred to as 'batch-continuous' since in essence a single batch is manufactured at a time. For long-run products, a truly continuous plant would be suitable, such as that illustrated in Figure 39.28. In this case, the addition of second vessels A′ and B′ (which are exact duplicates of A and B respectively) together with the three-way valves V_1 and V_2 means that a second batch of each phase can

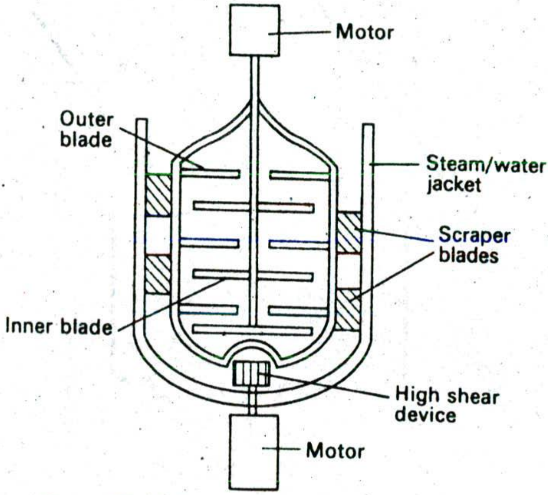


Figure 39.26 Batch emulsion processing plant

be prepared while the first is being used. In this way, a continuous supply of each phase is assured by the turning of a valve. In reality, continuous plants tend to be slightly more complex than is illustrated in the diagrams with the inclusion of take-off points for sampling and other sophisticated features. Nevertheless, continuous manufacture is a very practical and, for some applications, extremely economical method of processing emulsions.

Emulsion Temperature. The primary reason for raising the temperature of the phases during emulsion manufacture is to ensure that both are in the liquid state. In particular, the oil phase may contain fats and waxes that are solid at room temperature; there is very little point in raising the temperature of the oil phase much above that at which these liquefy. Excessive heating of the phases during manufacture prolongs the manufacturing time and wastes energy.

If the water phase is liquid at room temperature, it is customarily heated to approximately 5°C above the temperature chosen for the oil phase (so as not to cause the sudden solidification of the latter on blending). There is, however, an interesting alternative—namely, emulsification between hot oil phase and cold water phase. The plant for this procedure is illustrated in Figure 39.29, which shows that mixing of the phases and homogenization take place simultaneously. The obvious advantage of such a method is the saving of time and energy in not having to heat the aqueous phase.

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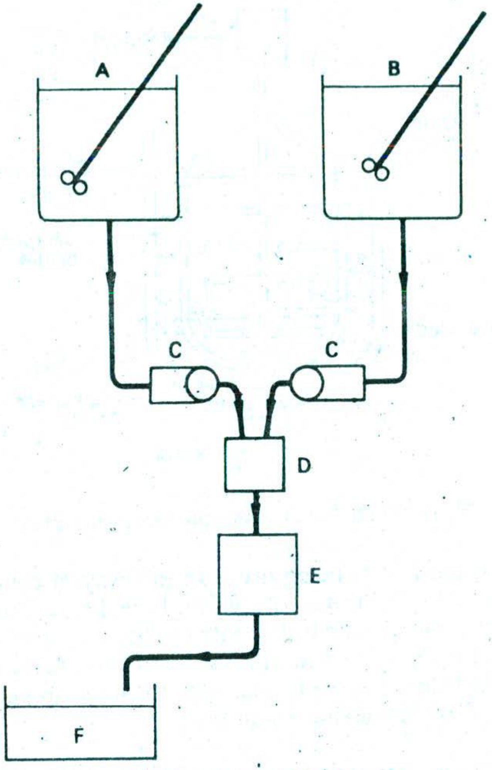

Figure 39.27 Simple continuous-processing emulsion plant
The two phases are prepared separately in tanks A and B, then pumped in correct proportions via metering pumps, C, into an in-line premixer, D (such as a static mixer), and then through a homogenizer, E. Finally, the formed emulsion is pumped into F, which may be a storage tank or the hopper of a filling vessel. A heat exchanger can be incorporated between E and F for rapid cooling

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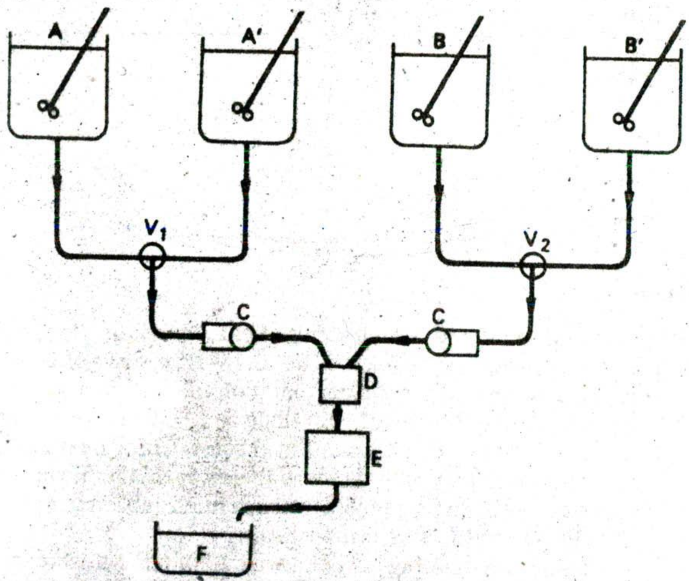

Figure 39.28 Continuous-processing emulsion plant for long-run products

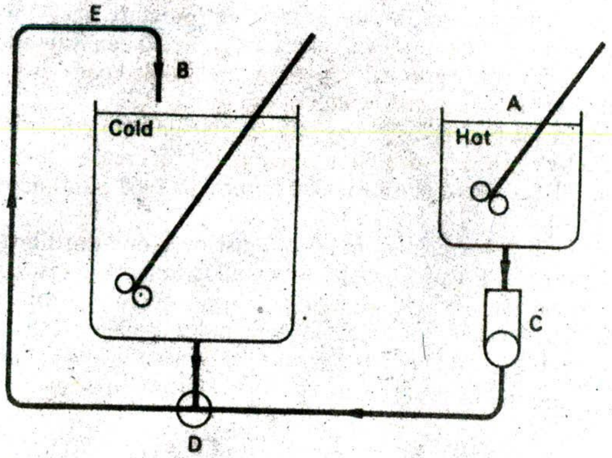

Figure 39.29 Hot/cold processing emulsion plant
The hot oil phase from tank A and the cold water phase from tank B are pumped into an in-line homogenizer at D and thence into the main tank B at E

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Chapter Forty

Aerosols

Introduction

Despite the fact that there had been a series of patents relating to the packaging of products under pressure going back as far as 1899,[1] it was not until the 1940s that the principle was applied for the presentation of consumer goods. In 1943, as a result of research on pest control, Goodhue and Sullivan were granted a US patent[2] for a portable aerosol dispenser, in the form of a heavy gauge metal container filled with insecticide and dichlorodifluoromethane having an internal pressure of approximately 70 psig (483 kPa). These portable aerosols were used at the time by the United States armed forces.

In 1947, USA statutes relating to pressurized containers were modified to permit the use of thin-walled containers more suitable for the consumer market. A rapid development of containers and valves then followed, giving rise to a new packaging industry. Because the parent pack (the wartime insecticide) dispensed its product as a true aerosol, all the descendant pressure packs, irrespective of the physical form of the product dispensed, have been subsequently called 'aerosol'. While for many products the term 'pressurized pack' is more accurate, the original designation is still widely used.

The new form of packaging enjoyed a spectacular growth rate. Thus in the USA a market of just over 5 million units in 1947 increased to 2000 million in 1967. World fillings[3] were close to 4000 million in 1968, and increased to 6000 million in 1978.

Over 6500 million were filled in 1980,[4] just over one-third in the USA and another one-third in Europe. In these two geographical areas, personal products—mainly hair sprays and deodorant/antiperspirant—form just over half the market, with household products (insecticides, polishes and air fresheners) forming the majority of the remainder. For the rest of the world insecticides are predominant but most future growth is expected in personal care products.

THE AEROSOL

Every aerosol consists of a gastight container, a valve closure, an actuator button and a protective cap; in the majority of packs dip tubes are present.

The operation of an aerosol is based on the discharge of its contents by the pressure of a compressed gas or the vapour phase generated by a propellant present in the container as a liquid. The container may be constructed of metal, glass or plastic, the most extensively used materials being tinplate and aluminium.

Valves differ in design and are mostly operated by downward finger pressure; some valves operating by a tilt action (sideways pressure) are also available. A dip tube which reaches almost to the bottom of the container is usually attached to the inlet side of valves to enable the liquid to flow to the valve when the container is in an upright position. Packs not fitted with dip tubes are intended to operate in an inverted position.

The design of the actuator button attached to the valve, particularly the shape and size of the orifice, largely determines how the product is dispensed. When the valve is actuated, the pressure inside the container forces the liquid concentrate through the dip tube, past the valve, into the actuator button and then out into the atmosphere in the form of a stream, mist, spray or foam.

CONTAINERS

Containers are available in tinplate and aluminium, plastic-coated glass and plastics. In America seamless drawn steel cans, usually internally lacquered and fitted with a tinplate base, can be found.

Tinplate

More than half of the world's aerosols are packed in three-piece tinplate containers with welded or soldered side seams. They are available in many sizes from 4 oz (150 ml) to 30 oz (1000 ml). The amount of tincoating applied varies with the component—body, cone or dome—and the country of origin, E2·8 (2·8 g m^{-2}) being common for bodies in America and Europe.

There are three types of solder generally used for making side seams:

1. The 2/98 tin/lead system (mixed solder or standard solder).
2. The Duocom (antimony/tin) system.
3. The 100 per cent tin system (plain solder).

The advantage of using plain (100 per cent tin) solder is that it does not give rise to the internal or external corrosion which may occur with mixed solder; however, because of its inferior mechanical strength it is liable to give rise to troubles at high internal pressures.

Only containers with welded seams are made now in the United Kingdom[5] and welding is gradually replacing soldering in other countries. The process is based on technology rather than craftsmanship and has therefore potential for further development. The weld is stronger than the body plate, allowing higher pressure formulations to be packed. The seam width is only a quarter that on soldered cans and thus it is possible to get nearly all-round decoration.

Aluminium

Aluminium cans are of two main types:

1. One-piece containers, the monoblocs, available in sizes of up to 36 oz (1200 ml).
2. Two-piece containers in sizes of up to 20 oz (750 ml).

These also differ in the neck profile, that of the monobloc being in the form of a rolled bead, while two-piece containers have solid beads which are not as consistent as rolled beads and are more prone to ridges and dents.

The two-piece cans have an aluminium body and a seamed-on base of either aluminium or tinplate. The latter type has the advantage of allowing the use of a magnetic water bath, but this is to some extent offset by a greater likelihood of corrosion. Both tinplate and aluminium frequently require protection from corrosion by the contents of the container. This is generally achieved by lacquering or, in the case of aluminium, by anodizing (see later in this chapter—Corrosion).

Uncoated Glass

Uncoated glass aerosol containers are attractive, with freedom of shape, but as a safety measure[6] only low pressures (between 15 and 20 psig; 103–138 kPa) should be used.

Plastic-coated Glass

The use of plastic-coated glass containers is restricted by pressure considerations. Vinson[7] recommended a PVC coating with a thickness of not less than 0·015 in (0·38 mm).

Valves for these containers are more expensive, since bottle valves are used instead of standard one inch valves and they are not produced in large quantities. The crimping method is different, and involves external crimping or swaging. The rejection rate of bottle valves is large. Advantages of glass packs are that they are non-reactive and cause no corrosion problems, since valves are not in contact with metal.

Selections of the various types of metal and glass containers available at present are illustrated in Figures 40.1, 40.2 and 40.3.

Plastic Packs

Plastic containers for aerosols are a more recent addition to this field of technology. They combine the advantages of safety and freedom from corrosion. However, they are rather expensive and in some cases interactions may occur between the perfume and the plastic or the plasticizer present. The plastic materials used include polyacetal and polypropylene.

Safety Considerations

Modern metal containers, especially those without a side seam, can be used with safety for pressures of up to 100 psig (690 kPa) at 21°C but glass packs containing liquefied gas propellants are only suitable for lower pressures. Even then they may require to have a metal, cardboard or plastic protective cover, which may be integral with the glass pack.

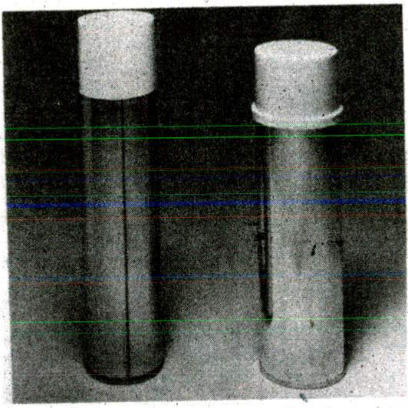

Figure 40.1 Tinplate aerosol containers
Trimline can with cover and Regular can with Top Hat cover
(Courtesy Metal Box Ltd)

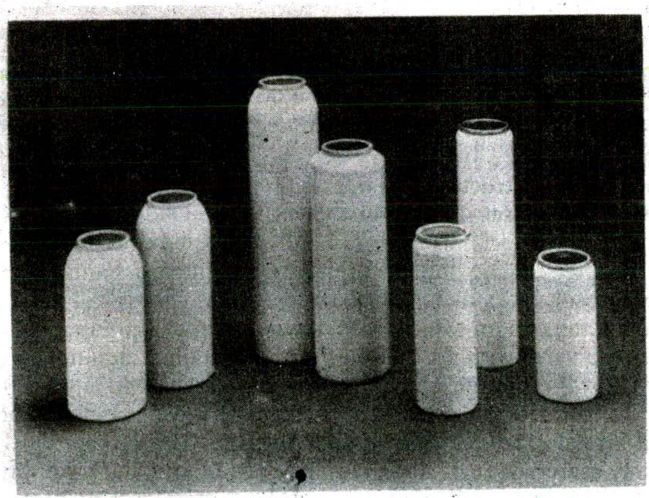

Figure 40.2 Aluminium aerosol containers

Figure 40.3 Glass aerosol containers
(Courtesy Max Factor Ltd)

VALVES

The most important part of the dispenser is the valve. There are many types of valve available, the major manufacturers being the Precision Valve Corp., Aerosol Research and Development, the Risdon Manufacturing Co., the Newman-Green Valve Co., Seaquist, Ethyl Corporation and Coster Tecnologie Speciali S.p.A.

The details of construction and operation of some of the main types of valve are outlined below (see Figure 40.4, p. 819).

The valve is the mechanism for discharging the product from the container, and in aerosol technology the term refers to the entire assembly which is sealed on to the aerosol pack, including the valve stem, spring and valve housing or body, the metal cup in which it is mounted, the dip tube (when present) connecting the valve with the contents of the container, and finally the actuator button or spray tip through which the product is discharged into the atmosphere. Figure 40.4 illustrates the intricacies of a typical valve assembly, and shows the propellant injection paths during the filling stage. The gasket, which may be of one of many materials (for example, nitrile, neoprene, butyl or Viton), plays a vital role in the operation of the aerosol and maintenance of pack integrity throughout its life. It is important, therefore, to apply deliberate care and attention to the correct choice of gasket, in order to achieve complete compatibility with the product and to ensure optimum valve performance. The valve determines the rate of discharge of the product, the form in which it is discharged—spray, foam, cream or powder—and, in the case of sprays, the fineness, the spray profile and spray pattern. By using metering valves, it is also possible to discharge a predetermined amount of product each time the valve is operated. The choice of valve and its various components is just as important in determining the success of the product as the selection of the propellant composition and the choice of product constituents.

Components

The basic components of the valve mechanism are:

1. The dip tube through which the product is delivered from the bottom of the container into the housing. It is usually made of polyethylene or polypropylene.
2. The valve housing or body which holds all the valve components together, and which itself is held in the mounting cup.
3. The valve, which transmits the product from the housing to the actuator button or spray tip and which acts as an expansion chamber.
4. The stem, a component of the valve, upon which the button is placed.
5. The gasket, which seals the stem orifice when the valve is closed.
6. The spring, which returns the stem to close the valve when the pressure upon the actuator button is released.
7. The actuator button (spray tip), which operates the valve and which controls product discharge. It can be made from various plastics, including nylon, polyethylene, polypropylene and acetal. The orifice size of the button will vary within a fairly wide range depending on the product to be dispensed.
8. The mounting cup, which is crimped around the housing and mounted on the container.
9. The cup lining or inner gasket, which is either flowed into, or placed in, the rim of the valve cup to form a seal when the valve cup is crimped over the neck of the container.

Operation

The presence of a compressed or liquefied gas in the sealed container gives rise to a pressure differential between the head space inside the container and the surrounding atmosphere. When the valve is opened, the product is pushed up from the base of the container through the dip tube into the valve housing, then through the open seal, up the valve stem, through the valve stem orifice into the expansion chamber formed by the valve stem and the actuator passage, and finally emerges into the atmosphere as a jet, or a fine or coarse spray or foam, depending on the design of the valve and actuator button, as well as on the propellant system.

Types of Valve

There are many types of valve designed to meet various specialized needs and purposes. Some of the variations are described below.

Standard Valves

These valves are designed to fulfil the function of controlling the discharge of the product from the container in a simple on–off manner by breaking or making a seal within the valve. The rate of discharge is governed by either the orifice at the seal or that at the final exit, whichever is the smaller, and this can be selected according to requirements. There are several variations of mechanism which come within the description of standard valves; these include vertical or tilt action buttons, integral or separate movable valve stems, and various designs of springs and seals.

Foam Valves

The valves used for dispensing foams are essentially standard valves fitted with wide unobstructed passages on the exit side of the seal orifice. This passage, which ends in a foam spout, serves as the expansion chamber in which the foam forms. The type of foam is governed by the composition and proportions of product and propellant.

Powder Valves

These also are little different from standard valves and the principal requirement is a smooth flow passage on both sides of the valve seal for the slurry of powder and propellant, so that there is a minimum possibility of powder deposition to interfere with the valve operation. Correct choice of powder ingredients and propellant is essential.

The Risdon Company[8] claimed to have overcome the problem of valve blockage by powders by means of a 'slide-and-clean' valve in which the internal metering orifice is in a movable stem, and which cleans itself by passing through the seal each time the actuator button is released. The stem wall carrying the orifice is thin so that the powder film in the orifice is disrupted by the pressure when the valve is opened. A number of other valve companies, notably the Precision Valve Corporation, successfully introduced long-stroke valves to prevent powder build-up and blockage of the orifice.

Mechanical Break-up Spray Valves

The standard valve serves primarily to open and close the container to the atmosphere and has no special provision for breaking up the product other than the vaporization of the propellant. Additional break-up can be provided by means of an expansion or swirling chamber in the actuator button. The product, with its flow accelerated by means of a constriction, passes into the chamber tangentially so that it moves in a spiral fashion, and the droplets break up by collision with each other and with the chamber walls before leaving the chamber through a small orifice, at high velocity.

Harris and Platt[9] pointed out that a product leaving the actuator in a neat condition will form a wide hollow cone, while if it still contains a proportion of miscible propellant it will form a narrower solid cone.

Break-up valves are used for dispensing aerosol perfumes and for hair lacquer, particularly those based on propellant 12 only.

Valves for Water-based Sprays

Water-based sprays with hydrocarbon propellants, for example insecticides and air fresheners, tend to require more intense break-up. This can be provided by special valves which have two entrances to the chamber in the valve housing. One entrance, the vapour phase tap, admits propellant vapour and the other, which is constricted, admits the product via the dip tube, which may be capillary. The restricted orifice is necessary to prevent propellant vaporizing in the dip tube, which would cause cavitation in the liquid. The stem has a large internal orifice to lead away the expanded volume of droplets and vapour.

Metering Valves

When it is desired to dispense a fixed amount of product for each actuation of the button, this is achieved by providing a chamber with sealed entrance and exit orifices. With the button in the closed position the metering chamber exit is closed and the entrance open, thus allowing the chamber to fill from the container. Depression of the button closes the entrance, trapping a metered volume of product (usually of the order of 50 μl) and then opens the exit to allow the escape of the product for use.

Controlled Discharge Rate Valves—Vapour Phase Taps

A valve is basically an on–off mechanism but it is sometimes possible to control the amount discharged, either by means of the extent to which the actuator is depressed or by using a variable discharge valve. The restricting orifice in a standard valve is usually the internal metering orifice, which normally has a diameter of not less than 0·010 in (0·254 mm).

Lower discharge rates can be secured by the following methods:

1. Replacing the normal dip tube (bore about 0·15 in or 3·8 mm) by a capillary tube with bore 0·04–0·10 in (1·01–2·54 mm) or microcapillary of 0·014–0·017 in (0·35–0·43 mm).
2. Using a low-delivery housing in which the orifice at the bottom of the housing is restricted to 0·008–0·025 in (0·02–0·63 mm).
3. Using a vapour phase tap. This is a small orifice in the side of the housing, connecting the head space of the container with the inside of the housing, for introducing propellant vapour into the valve at this point. It may be used to improve break-up (*cf.* the valve described under 'water-based sprays') or to allow a rapid return of the liquid phase left in the dip tube and minimize possible blockage by products containing dispersed solids. A vapour phase tap has advantages in that:

    (i) it allows the aerosol to be operated in both upright and inverted positions, when the propellant and product each enter the housing through the orifice normally serving the other;

    (ii) it lessens the cooling effect by reducing the discharge rate and by reducing particle size, which accelerates evaporation before the spray reaches the target area;

    (iii) it allows faster filling in the presence of a low-delivery housing which normally demands under-cup fillling, except with the new generation of valves.

The vapour phase tap may, however, result in the loss of too much propellant from the head space with the risk of incomplete discharge of the product, or a changed spray pattern as the container is emptied. This can be prevented by ensuring that the tap is of a suitable size and that there is an adequate amount of propellant present.

Fast Filling Valves

From the 1970s and into the 1980s the requirement remains for valves that allow even faster filling of the aerosol container. This has come about partly because of changes in propellant and requirements for lower discharge valves, and partly because of a need to increase output speeds of production lines. A number of valve companies, notably the Metal Box Company, UK, with their CL-F valve, have developed systems whereby propellant may also by-pass the discharge path during the filling operation and thus ensure fast gassing no matter what the size of the internal orifices within the valve. Such valves may be used also for direct injection of compressed gases into standard cans using standard equipment.

Transfer Valves

These valves are used to provide a connection with smooth flow between the stems of two standard valves with their buttons removed. They are used for recharging the smaller daily use pack of, for example, 'mother and daughter' pack hair lacquers, for refilling cigarette lighters with liquid butane and in the laboratory for pressurizing aerosol cans with propellant from other cans.

Speciality Valves

An innovation in 1968 was Risdon's valve which was designed to work effectively in any position, from upright to inverted, without loss of vapour gas.[10] The valve has, in addition to the usual assembly, a double dip tube with a transfer connection opened and closed by a ball valve to allow the product to flow between the tubes as the container is tilted. It is claimed that the valve can be used with all types of propellants and with any actuator.

PROPELLANTS

The distinguishing and essential feature of an aerosol is the propellant, which may be a liquefied gas (which will vaporize at atmospheric pressure), a compressible gas or a mixture of the two.

Liquefied Gas Propellants

The majority of aerosols employ liquefied gas propellants, that is propellants which are in the gaseous state at atmospheric pressure and room temperature, but which liquefy on compression. When liquefied, their vapour pressure will vary with temperature. The high vapour pressures of some of the lower boiling compounds must be reduced, by the use of pressure depressants, so as to achieve pressure compatibility with common aerosol containers and also to impart consumer-acceptable spray characteristics.

The important feature of a liquefied gas propellant, distinguishing it from compressible gases, is that as long as any propellant is still present in the pack in its liquefied form the internal pressure within the container will, at any given temperature, be constant irrespective of how much product or propellant has been discharged. As the head space in the pressure pack increases, more of the liquid propellant evaporates to maintain the internal pressure at an approximately constant value. This ensures that the spray characteristics of a pack are virtually unchanged, irrespective of whether the package is full, half-full or almost empty, and hence ensures consistent performance throughout the life of the aerosol. Of course the temperature of usage affects spray performance.

Spray characteristics differ at extremes of temperature, because they are directly affected by pressure which is temperature-dependent. The normal leakage experienced through valves and seams of sound aerosols is increased at higher temperatures. At very high temperatures deformation and rupture may occur under the influence of the attendant high internal pressures.

Liquefied gas propellants include chlorofluorocarbons, hydrocarbons and dimethyl ether.

Chlorofluorocarbon Propellants

The most important chlorofluorocarbon propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, and their mixtures.

In addition to the 'Freons' of E. I. du Pont de Nemours Co., USA, who were the first to produce them on the commercial scale, trade names under which these products are sold include:

Algofrene (Montecatini Societa, Italy)
Arcton (Imperial Chemical Industries Limited, UK)
Forane (Elektrochimie Ugine, France)
Frigen (Hoechst Chemicals, Germany)
Isceon (ISC Chemicals Limited, UK)

An international code is used for the various chlorofluorocarbon compounds, and is interpreted as follows:

(i) The right-hand number represents the number of fluorine atoms.
(ii) The second number from the right represents the number of hydrogen atoms +1.
(iii) The third number from the right represents the number of carbon atoms −1.
(iv) Spare valencies are filled by chlorine atoms.
(v) The fourth number, if present, is the number of double bonds, and a prefix C indicates that the compound is cyclic.
(vi) Conversely, if 90 is added to the code number, the last three digits, starting from the right, give the number of fluorine, hydrogen and carbon atoms respectively, with chlorine atoms to make up the valency requirements.

Details of molecular weights, vapour pressures and boiling points for the three most commonly used chlorofluorocarbon propellants are given in Table 40.1.

Propellant 12 may be used on its own, without auxiliary pressure depressants, as for feminine hygiene sprays. It is more usual to associate this propellant with

Table 40.1 Properties of Chlorofluorocarbon Propellants

Propellant	International Code No.	Chemical formula	Molecular weight	Boiling point	Vapour pressure at 21°C (psig)	(kPa)
Dichlorodifluoromethane	12	CCl_2F_2	120·9	−29·8°C	70·2	484
Trichlorofluoromethane	11	CCl_3F	137·4	−23·8°C	13·4	92·5
Dichlorotetrafluoroethane	114	$C_2Cl_2F_4$	170·9	+ 3·6°C	12·9	88·9

pressure depressants deliberately incorporated into the product formulation or occurring there naturally to achieve lower internal pressures compatible with commonly available containers.

The traditional pressure depressant propellant 11 may, under certain conditions, cause corrosion of metal containers in the presence of water or the lower alcohols. In these circumstances or where there is an adverse effect upon certain perfumes, it is advisable to replace it by propellant 114. Propellant 114 is extremely stable; it exerts a low pressure of about 13 psig (90 kPa) at 21°C, and this makes it generally unsuitable for use on its own in temperate climates.

By mixing propellants 11, 12 and 114, all practically required pressures may be obtained. Since these mixtures obey Raoult's law, their pressure characteristics can be predicted. If, however, they are mixed with other types of propellants or with solvents (for example ethanol) the resulting mixtures will deviate from Raoult's law.

The most commonly used propellant mixture contains equal parts by weight of propellants 11 and 12 and exerts a pressure of about 37 psig (255 kPa) at 21°C; it is used in such applications as solvent-based space insecticides and air fresheners. Mixtures in different ratios will give rise to different pressures more suitable for hair sprays, deodorants and antiperspirants. Mixtures of propellants 12/114 in weight ratios ranging between 10/90 and 40/60 are used to pressurize products such as shaving creams, colognes and perfumes.

Vapour pressures exerted by various mixtures of propellants 11 and 12 and propellants 12 and 114 at 21°C are given in Table 40.2.

Chlorofluorocarbons 11, 12 and 114 are characterized by a high degree of stability and a low order of toxicity; studies on the possibility that chlorofluorocarbons may be toxic if inhaled have been reviewed in Chapter 25 under the heading of Hair Sprays. They do not form explosive mixtures with air. They are also nonflammable and furthermore they depress the flammability of aerosol formulations which include flammable solvents.

The Chlorofluorocarbon Ozone Controversy. The hypothesis that emissions of chlorofluorocarbons to the atmosphere would cause depletion of ozone, and thus increase the amount of harmful UV radiation reaching the surface of the earth, was first postulated by Rowland and Molina in 1974.[11] Since then a great deal of research effort has been applied in attempts to validate the theory. While this has increased our knowledge, it has shown that our understanding of the

Table 40.2 Vapour Pressures of Mixtures of Propellants

Propellant mixture 11/12 ratio by weight	Vapour pressure at 21°C (psig)	(kPa)	Propellant mixture 114/12 ratio by weight	Vapour pressure at 21°C (psig)	(kPa)
70/30	23	158	90/10	20	138
65/35	27	186	85/15	24	165
60/40	30	207	80/20	27	186
50/50	37	255	70/30	34	234
40/60	44	303	60/40	40	276
35/65	47	324	50/50	46	317
30/70	51	352	40/60	51	352

atmosphere is very much less complete than had been assumed. The atmosphere is being revealed as a very complex interlinked system and the consideration of a single effect or reaction sequence in isolation can give very misleading results.

Numerous reports, for example that by Brasseur,[12] have been written reviewing the scientific developments together with calculations of potential ozone depletion. Such calculations, which are based on many assumptions, may be regarded as doubtful forecasts as they are a compound of uncertain science and uncertain scenarios projected many decades ahead. Research into the problem continues and new assessments of the science are prepared as more information becomes available.

Statistical treatment of actual ozone measurement data has so far failed to reveal a depletion trend.

Notwithstanding the lack of scientific validation of the Rowland–Molina theory, some countries have regulated the use of chlorofluorocarbons as aerosol propellants.

Hydrocarbon Propellants

Hydrocarbons such as propane, n-butane and isobutane, which have a low order of toxicity,[13] are used in aerosol packs as cheap, stable and non-corrosive propellants which are handled safely in transport, storage and filling operations.[14–16] They are used with water-based products to give low-cost non-flammable end products that present no special corrosive hazards. They are blended with other propellants and solvents to lower the overall costs and in some cases actually improve the product.

These hydrocarbons, which must be relatively free of impurities, may be blended with each other or with the chlorofluorocarbons to give the required vapour pressures for the propellant charge content to dispense aerosol products satisfactorily.

Propane, n-butane and isobutane are the only naturally occurring hydrocarbons which have the stability and availability that make them suitable for use on a commercial scale. These hydrocarbons are readily separated from naturally occurring mixtures to give stable odour-free propellants in large volume at low cost. Their physical properties are given in Table 40.3. Hydrocarbons are used alone in water-based aerosol products such as shaving creams, window cleaners,

Table 40.3 Physical Properties of Hydrocarbon Propellants

Propellant	Specific gravity of liquid	Formula	M.W.	Boiling point at 1 atm (°C)	Vapour pressure at 100°F (37·8°C) (psig)	(kPa)
Propane	0·508	C_3H_8	44·09	−42·1	189·5	1306
n-Butane	0·584	C_4H_{10}	58·12	−40·5	52·0	358
Isobutane	0·563	C_4H_{10}	58·12	−11·7	73·5	507

air fresheners and spray starches. They may also be used alone or combined with other propellants to dispense many water-free products.

Hydrocarbons with their low specific gravity are lighter than most products so the liquefied hydrocarbons will float on top of the product when they are immiscible.

Herzka[17] has indicated that there are advantages in using propellants that are lighter than the product; in particular there is no danger of discharging pure propellant with three-phase systems, at least until all the product has been dispensed.

Besse, Haase and Johnsen[18] have presented graphs showing that up to 30 mole per cent of propane can be blended with propellant 12 before a pressure of 100 psig at 70°F is reached (689 kPa at 21·1°C).

Smaller amounts (about one-third by weight) of hydrocarbon propellants, because of their lower specific gravity, are required compared with chlorofluorocarbon propellants in order to give the same pressure in an aerosol container and to give the same volume content in a formulation.

The hydrocarbon propellants are soluble in chlorofluorocarbons, alcohol, chloroform, methylene chloride, ether and the higher hydrocarbons such as n-pentane and n-hexane. They are non-polar and are not hydrolysed by water. There is little chance of the formation of corrosive substances from the hydrocarbons. This non-corrosive characteristic is an important advantage in the use of hydrocarbons in aerosol propellants. They are also essentially immiscible with water. Butane–water–alcohol systems, designed to produce a single liquid phase, are of increasing importance for personal care products such as hair sprays. Care needs to be exercised with respect to corrosion and therefore product/container compatibility.

Hydrocarbon propellants have a low toxicity rating, and they do not form toxic decomposition products at high temperatures. Normal care should be exercised, however, to avoid contact of the liquid with the skin or eyes.

Hydrocarbons have low flash points and low explosion limits.

	Flash point (°C)
Propane	−104
Butane	−74
Isobutane	−83

However, from the point of view of flammability the properties of the complete formulation are most important. Many formulations using hydrocarbons as the sole propellant and many containing a combination of halocarbons and hydrocarbons are also non-flammable. Components of an aerosol mixture other than the propellant, such as solvents, resins, etc., may increase flammability risks.

Many examples of non-flammable products containing hydrocarbon propellants have been reported in the literature. Other instances have been reported in which the presence of hydrocarbon in the propellant actually reduced flammability.

Reed[19] described a propellant comprised of:

	per cent w/w
Propellant 11	45
Propellant 12	45
Isobutane	10

Similar blends are being brought into use increasingly for alcohol-based hair sprays and deodorants.

Fowks[20] cited an example in which the length of the flame in flame extension tests was notably reduced when a chlorofluorocarbon propellant in a hair spray was replaced by a chlorofluorocarbon–hydrocarbon mixture.

Calor Gas (Limited) UK supplies propane–butane mixtures now used as propellants in a large number of important aerosol products. They offer 'destenched gas' as opposed to 'unstenched gas'—the latter being collected at the refinery and containing a small quantity of residual sulphur compounds.

Destenched gas is obtained by further processing through molecular sieves or other absorbents. Calor aerosol propellant is available as a standard at pressures of 30, 40, and 48 psig (207, 276 and 331 kPa) at 21°C. The different pressures are obtained by varying the percentages of butanes and propane present, since each has a different vapour pressure.

Dimethyl Ether

Rotheim, in Norway, first suggested the use of dimethyl ether for aerosols.[21] Since 1966, aerosols using dimethyl ether as a propellant have been produced, with the major contribution from Holland.

Highly purified dimethyl ether is an attractive propellant.[22,23] It is virtually odourless, has specific dissolving powers and, as it is miscible with water, is capable of producing single liquid phase product systems (with ethanol, for example) thus commending its application to various personal care products.

Current toxicological studies,[24] wide in their scope, provide encouraging data to date. The toxicity studies continue and further data are awaited with interest.

Flammability characteristics of dimethyl ether are such that when it is handled with appropriate caution and care, both in production and in product formulations, commercial experience reveals that no unacceptable hazard is posed.

Increasingly dimethyl ether is being used both in Europe and now in America for many types of aerosol product, including hair sprays, setting lotions, deodorants, deo-colognes, perfumes and toilet waters.

Compressed Gas Propellants

The use of compressed gases as propellants for pressurized packs was first proposed in the second half of the nineteenth century—well before the introduction of chlorofluorocarbons.[25,26] The term 'compressed gas aerosol propellants', as far as the aerosol field is concerned, is applied to gases that can be liquefied only at very low temperatures, or under extremely high pressures. The compressed gases mostly used as propellants are nitrous oxide, carbon dioxide and nitrogen.

Before 1958 the use of carbon dioxide and nitrous oxide was introduced for whipped cream aerosols, while carbon dioxide alone is used for de-icers and fire extinguishers. It was only after special valves became available that it was possible to use nitrogen as the propellant for dispensing toothpaste, thick emulsions in stream form, and various liquids in spray form, for example, perfumes in glass bottles.

There are a number of differences in behaviour, connected chiefly with volume and pressure changes, between compressed gases on the one hand and liquefied propellants on the other, and even in some respects between compressed gases that are soluble in the product and those that are not. These differences produce different performance characteristics in aerosols. Some of the differences are listed in Table 40.4.

In practice, nitrogen is used for dispensing products in an unchanged form. An extension of this principle is illustrated by the free piston aluminium aerosol can developed by the Bradley Sun Division of the American Can Company.[27] This provided a true solid-stream dispensing of the product which was separated from the propellant by means of an internal plastic diaphragm made from medium density polyethylene. The propellant was nitrogen, introduced at 90 psig (620 kPa) through an aperture in the concave base of the can, which was then immediately closed with a rubber plug. The pressure of nitrogen caused further compression of the walls of the piston against the can, thus providing a seal which prevented mixing of the product and propellant. The piston was free to move up and down within the container as the pressure on either side changed. An almost complete (99 per cent) discharge of product was achieved.

Carbon dioxide used alone gives a wet product and a large fall-off in pressure leading to changed discharge characteristics and possible unexpelled product. Large head spaces, which invite adverse consumer reaction, tend to reduce these problems slightly. With aqueous products there is a possibility of product reaction and also of corrosion, which necessitates the use of special valves and cups. A system developed in Germany, the Carbosol system,[28] relied on the fact that at a given temperature and pressure a liquid absorbs a given quantity of carbon dioxide. Facilities for saturation of solvents to be used in a special Carbomix or Carbomat reactor were provided. Although this system on the face of it offered an alternative to the conventional propellant system, no significant commercial success was achieved.

Mixed Compressed Gases and Solvents

Mixtures of carbon dioxide with chlorofluorocarbon have been proposed, and although pressures are higher (60–70 psig or 414–483 kPa) they can usually be

Table 40.4 Comparison of Compressed Gas Propellants and Liquefied Propellants

Characteristics/Properties	Compressed gas propellant		Liquefied propellant
Solubility in product	Insoluble	Partly soluble	Partly soluble
Example	Nitrogen	Carbon dioxide	Chlorofluorocarbon or hydrocarbon
Pressure effects	Decreasing pressure as product is used, with decreasing discharge rate, changing spray pattern, and product retention, especially if volume fill of container high.		Constant pressure throughout use of pack, with constant discharge characteristics and low product retention.
Product residues	Tend to be high although less with soluble propellants.		Generally low.
Volume changes on discharge to atmospheric pressure	Gas not discharged with product, so no break-up effect, except that imparted by special break-up actuators.	Gas dissolved in product under pressure escapes with a 10-fold volume increase. Break-up effect small but significant. Correct choice of valve specification very important.	Propellant in formulation vaporizes with a 250-fold volume increase. Consequently large break-up effect which can be enhanced still further by correct choice of valve and, especially, the actuator.
Pressure change with temperature rise	Propellant largely obeys gas laws and shows small pressure changes with temperature.		Propellant is not an 'ideal' gas and shows considerable pressure change under influence of temperature.
Effect when product sprayed on skin	No chilling.	Slight chilling.	Marked chilling effect due to heat required for vaporization.

safely used with tinplate and aluminium cans. Filling presents difficulties, and has to be carried out as a two-stage process which slows down production, or else by special methods such as pre-saturation of the product with carbon dioxide. However, new generation valves may be employed which avoid all of these difficulties.

Both nitrous oxide and carbon dioxide have been used in conjunction with chlorofluorocarbon for dispensing space sprays.

Another mixed propellant system, developed by the Dow Chemical Co., is based on a mixture of a soluble compressed gas such as nitrous oxide with chlorinated hydrocarbons such as methylene chloride or 1,1,1-trichloroethane. This system is claimed to be cheaper than the chlorofluorocarbons which are replaced either in part or totally.

Depending on the solvency of the mixture and nature of spray required, the chlorinated hydrocarbon may be methylene chloride or 1,1,1-trichloroethane or blends of the two in the range 1:2 to 2:1. Grades of 1,1,1-trichloroethane developed for cold degreasing or vapour degreasing are generally applicable to aerosol use, for example:

Genklene N	ICI Ltd
Genklene LV	
Chlorothene NU	Dow Chemical Co.
Chlorothene VG	

The following examples illustrate hair spray formulations based on this system:

	(1) *per cent*	(2) *per cent*	(3) *per cent*
Methylene chloride	15	15	16
1,1,1-trichloroethane	10	31	16
Propellant 12	25	—	16
Nitrous oxide (60 psig, 414 kPa)	—	—	2
Nitrous oxide (80 psig, 551 kPa)	—	4	—
Hair spray concentrate	50	50	50
Perfume	*q.s.*	*q.s.*	*q.s.*

Methylene chloride and 1,1,1-trichloroethane are exceptionally good solvents for compressed gases, thus ensuring good filling characteristics and spray break-up while minimizing product residues.

With such solvent–compressed gas systems aerosols are filled to about 80 psig (551 kPa), and it is claimed that a pressure drop of 30 psig does not result in any appreciable change in spray quality if the valve system is suitably chosen to give the required spray characteristics. It has been found that such aerosols will deliver the product at a rate 60 per cent faster than a container using liquefied propellant at 40 psig (276 kPa).

Use of Methylene Chloride and 1,1,1-Trichloroethane

Methylene chloride and 1,1,1-trichloroethane are being used as solvents in aerosol hair sprays, insecticides, air fresheners, paints, oven cleaners and lubricants.

These solvents function as co-solvents for active ingredients and propellants and vapour pressure depressants. They are non-flammable under normal conditions and so help to control flammability and flammable contents within prescribed legal limits. The high densities of the two solvents provide mass compensation when used with low density propellants.

They are available in stabilized forms to give good performance in the presence of moisture, heat, light, metals and air.

Chlorinated solvents are usually non-corrosive when used in anhydrous aerosol formulations. Some hydrolysis may occur, however, in the presence of water, similar to that experienced with some chlorofluorocarbons.

The use of special inhibitors to protect against corrosion has been suggested. The results have been published[29] of tests showing superior properties in respect of corrosion of tin, steel and solder. However, it is recommended that water-based aerosols should be thoroughly shelf tested before marketing—this is sound advice for any new or modified aerosol product.

Once the balance of solvents to produce the required spray characteristics from the total formulation has been established, the choice of gasket should be carefully made, as with any new product formulation.

Gelled Propellants

When a product is dispensed from a conventional aerosol container, some of the liquid propellant is included in the spray. The additional droplets of liquid propellant can cause non-uniform deposition of product, a more rapid change in the characteristics of the spray during long bursts owing to cooling caused by evaporation of propellant, and increased cooling effect on skin with such products as antiperspirants and deodorants. It has been claimed[30] that these undesirable effects are minimized by the use of gelled versions of any liquefied propellants. The propellant mixes with the solution of the product in its dry vaporized form, and additional liquid droplets are not introduced into the spray.

The initial spraying times of gelled propellants were claimed to be approximately one-third greater than those of conventional propellants, and the overall dispensing capacity was said to be approximately 40 per cent greater than that provided by the conventional types of propellant.

FILLING OF AEROSOLS

As the industry began, the most important method for filling aerosols with liquefied propellants was cold filling. This method is still used today for some specialized filling, particularly in the perfume and pharmaceutical industries.

A second important method—under-cup filling—became a dominant method of production filling aerosols in the late 1960s and the 1970s in the United States, using machines from Kartridg Pak, USA. It was also adopted, particularly for large filling operations, in other countries.

With ever increasing importance, pressure filling is the most important production method employed world-wide today. Eminently suitable for liquefied propellants of all types, it is now also accepted as a proven method for compressed gases provided that suitable aerosol valve designs, originating in the 1970s and improved in the 1980s, are employed.

Cold Filling

In cold filling, the propellant is cooled to a low temperature at which it will handle as a liquid, and is run through the open aperture of the aerosol container to join chilled product concentrate already there. The valve assembly is then sealed on to the container.

This method facilitates the rapid filling of propellant while at the same time expelling air from the aerosol container. It cannot be used where the chilling effect produced by the addition of the cold propellant would adversely affect the product concentrate as, for example, with some emulsions and water-based products.

The temperature of the contents in the sealed aerosol container soon returns to normal, assisted by passage through the essential hot water test bath.

In spite of the simplicity of the cold filling method, both capital investment costs and refrigeration running costs are high.

Under-cup Filling

All operations in under-cup filling are conducted at ambient temperatures. Product is filled into the open-aperture container. The valve, complete with actuator, where dimensions allow, is placed loosely in the one inch (25·4 mm) aperture and the filling head is lowered to seal over and around the container top.

The valve is lifted slightly, a vacuum is drawn in the container head space, and propellant is injected between the valve and the can curl. Then the valve is sealed into the container aperture and the filling head recedes.

Pressure Filling

With pressure filling, the propellant at room temperature is injected under pressure through the aerosol valve itself (see Figure 40.4).

The sequence of operations entails the addition of the concentrate to the empty container, displacement of air from the head space, sealing on the valve assembly, metering the required quantity of propellant and injecting it under pressure through the aerosol valve.

With cold filling, the introduction of propellant into the open container displaces almost all the air in the head space. It is a self-purging operation. However, when pressure filling is used, there is a seal between the charging head and the aerosol valve; air remaining inside the container could not escape and would be compressed as the propellant was added. This air would contribute to undesirable excess pressures in containers and the oxygen in the air would affect corrosion performance. Therefore it is necessary to evacuate the head space by vacuum closing the valve on to the container, or by using an appropriate method of purging.

Pressure filling machines employ pneumatic or hydraulic systems to operate the charging cylinder. The quantity of propellant is varied by the adjustment of

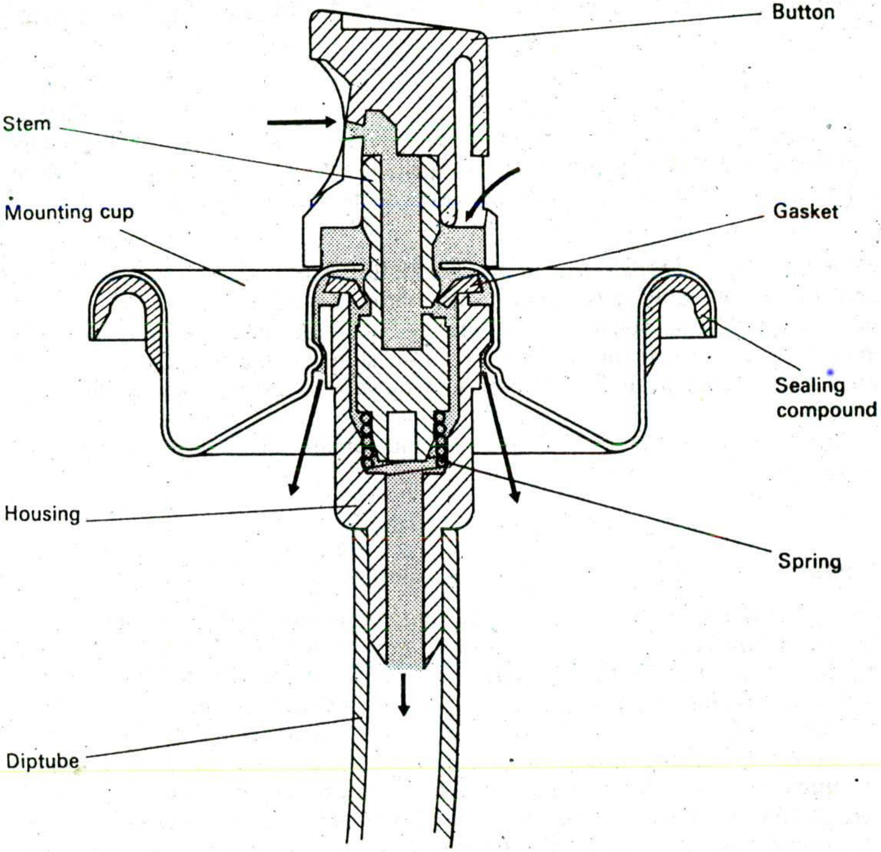

Figure 40.4 The CLF valve with 2000 series button
The valve is mounted in a metal mounting cup which can be swaged (clinched) into the one-inch aperture of the container. It is shown in the open position with the spring compressed and the gasket depressed, and with an indication of the propellant injection flow paths during pressure filling (Courtesy Metal Box Ltd)

the stroke of the charging piston. The filling head on the valve is opened mechanically or by propellant pressure, or both, to permit propellant injection to take place.

Rapid injection even when there is a high propellant charge is possible with current valves, irrespective of specification.

Pressure Filling Variants
There are several variants of the actual process of pressure filling the propellant. These variants include:

Pressure Filling with Button off. After the valve has been sealed into the container aperture, propellant is injected through and around the valve stem. Then the actuator button is fitted.

Pressure Filling Around the Button. The button is in place on the valve which is closed on to the container. The filling head makes a seal concentrically on the cup boss, and the injection of the propellant into the container takes place primarily between the stem and the hole in the valve cup boss.

Pressure Filling Through the Button. The button is provided with gassing holes and the seal is made by the skirt on the button between the cup boss and the filling head. The propellant then enters the container through the gassing holes in the button and again primarily between the stem and the hole in the valve cup boss. Cups and stems may be chosen to achieve very fast production filling and line speeds.

Again, pressure filling is equally suitable for all liquefied and compressed gases.

Solvent Saturation

Solvent saturation is an alternative procedure for compressed gases which entails the pre-saturation, in a pressure tower, of part of the solvent used in the liquid product concentrate with a soluble compressed gas, to the desired pressure, before combining it with the balance of the concentrate in the container. This procedure offers an alternative to expensive gasser shakers and allows improved filling rates, making it attractive compared with other methods of filling compressed gases. This type of aerosol filling has been adopted by a number of aerosol fillers. However, the most important development in aerosol filling of compressed gases is their metered introduction into containers through the valves, using pressures and equipment similar to those employed for liquefied propellants—that is, impact gassing with the latest aerosol valves.

Free Space in an Aerosol

In any closed container completely filled with liquid, a rise in temperature will result in the development of hydraulic pressure which may deform and even rupture the package. Chlorofluorocarbon propellants have a high coefficient of expansion. However, in all aerosol containers allowance must be made for the expansion of the contents by provision of adequate ullage or head space. Also it is wise and common practice to make provision for testing all filled aerosols in a hot water bath, for example at 50°–55°C for metal aerosol containers, as a safety check and to permit removal of 'leakers'.

The consumer's requirement of maximum fill of product conflicts with the need for safety, that is, the avoidance of hazards to the consumer from excessive fills. In Europe, a general rule is becoming accepted of a 75 per cent product fill, and thus 25 per cent head space (or ullage) at 20°C.

Check Weighing

In production it is customary to weigh a proportion of the filled aerosol containers, in order to check the accuracy of the filling operation, and to ensure that filled units correspond with requirements.

Hot Water Bath Testing

After production filling and closing, metal aerosol containers are tested for leaks and checked for safety and integrity by immersing in a water bath at 50°–55°C. Similar arrangements are required for glass and other non-metal containers. In small-scale operations, a simple tank with a thermostat and immersion heater may be used, in which the containers are manually immersed using a wire basket. In large-scale filling, the containers are usually carried on a conveyor through the water bath. Safety protection is provided for operators. The testing area should be well illuminated to allow minute bubbles from a leak to be readily detected. After leak and safety testing, the residual water must be removed from the valve cups before the filled containers are packed into cartons. Air blast tunnel driers and similar devices are used for this purpose.

TYPES OF DISPENSED AEROSOL PRODUCT

There are two sides to an aerosol—the inside (the contents) and the outside (dispensed contents).

Inside contents of aerosols are either two-phase (gas and liquid) or three-phase (gas, liquid gas and liquid concentrate); the latter occurs when liquid propellant and liquid product lack miscibility.

Products can be dispensed in various forms (sprays consist of liquid and/or solid particles):

1. Space sprays (true aerosols) composed of minute particles which remain suspended in the air for long periods of time. Examples are insecticides and air fresheners.
2. Surface (wet sprays) with larger particles. Examples are hair sprays and deodorants.
3. Surface sprays as jets. Examples are de-icers and lubricants.
4. Foams in which the liquefied gas propellant is partially emulsified with the active components of the product; they may be stable or collapse readily and present various consistencies. Examples are soaps, shaving creams and suntan foams.
5. Original unchanged physical form; the product is dispensed with the same physical form as that existing inside the container. This is generally the conventional form in which it would be obtained from a non-pressurized container but in a more convenient form, for example a liquid cream or a ribbon of solid cream or paste. Toothpaste is an example.

TWO-PHASE SYSTEMS

A large proportion of all aerosols are two-phase systems containing a liquid and a vapour phase (Figure 40.5). When the actuator, or button, of the aerosol is

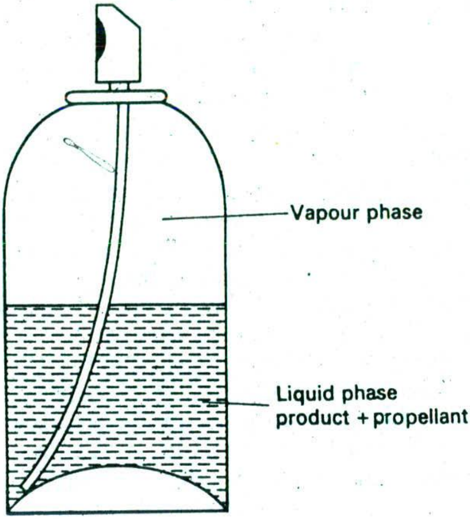

Figure 40.5 Two-phase aerosol system

pressed, the pressure inside the container causes the liquid to rise up the dip tube, through the open valve, and out of the button into the atmosphere where the lower pressure allows the immediate expansion and vaporization of the propellant and transforms the product into a spray mist, jet or foam. The solvent will also evaporate rapidly leaving behind the active constituents in a finely concentrated and dispersed form.

The majority of two-phase packs consist of a homogeneous solution of active matter, solvent and liquid propellant as the liquid phase, with propellant as the vapour phase. Compressed gases which may or may not be soluble in the liquid phase may also be used. The size of the emerging product particles is largely determined by the propellant/product ratio, and is influenced by the design of the valve. Examples of products based on two-phase systems are hair sprays, deodorants and colognes. Space sprays, air fresheners and insecticides of the solvent-based type are also two-phase systems.

The solvents employed in two-phase systems must effect a complete solution of all the active ingredients, for example hair spray resin in ethanol, so that the liquid phase of the filled pack is completely homogeneous. In addition to dissolving the active substance, solvents in two-phase systems must also be miscible with the propellant. Common solvents with these properties, and which show sufficiently low irritancy and toxicity when used topically or inhaled, include water, ethanol, isopropanol, propylene glycol and hexylene glycol. Other solvents include methylene chloride and 1,1,1-trichloroethane.

Space Sprays

Space sprays of the two-phase variety require high propellant/product ratios to achieve optimum particle size. Usually they contain not less than 80 per cent of liquefied gas propellant and consequently the amount of product concentrate is relatively small. The sprays emerging from such packs are true aerosols, with particle sizes of the order of 50 μm or less.

A good example of the functional use of space sprays is the aerosol room deodorant, which may be considered as bordering on a toilet preparation, and which must be atomized (as in the case of insecticides) in order to be effective. Such products may function by a number of mechanisms including the physical removal of malodours, by literally washing the air, by chemical neutralization or by an odour-masking or reodorant effect.

The formula given in example 4 functions primarily by the reodorant principle, but the glycols assist in the physical removal of malodours.

	(4) *per cent* *w/w*
Triethylene glycol	4·5
Propylene glycol	4·6
Ethanol	6·0
Perfume	0·2
Propellant 11	42·5
Propellant 12	42·5

Internal pressure at 20°C: approximately 40 psig (276 kPa).
Suitable container: tinplate.

Inexpensive hydrocarbon-propelled solvent-based insecticides based on two-phase systems are important worldwide. However, three-phase hydrocarbon-propelled water-based emulsions employing vapour-phase tap valves are important for insecticides and dominate the air freshener market for reasons of cost.

Surface Sprays

When the product constitutes 20–75 per cent by weight of the pack (with appropriate propellant loadings to complement), the resulting particle size of the sprayed product may be of the order of 50–200 μm. This type of spray, exemplified by hair sprays, is referred to as a surface spray because the particles are of such a size that they cannot remain suspended in the air but deposit and coalesce on the available surfaces to which they are applied. They are sometimes referred to as wet sprays, and include body deodorants, colognes, perfumes and suntan sprays.

These sprays are commonly of the two-phase type. Although alcohol-based products can be produced with a liquefied propellant concentration as low as 25 per cent, or even 5 per cent in the case of compressed gases, the resulting sprays are relatively coarse.

Other personal products may contain as much as 95–99 per cent propellant, for example feminine hygiene sprays, so chosen, in combination with a vapour-base tap valve, that the chilling/freezing effect is avoided.

Some surface spray products using two-phase systems are described below.

Hair Spray
Example 5 is a typical hair spray formula.

	(5) *per cent*
Resin	1·5
Soluble lanolin derivative	0·2
Isopropyl myristate	0·2
Perfume	0·2
Ethanol	32·9
Propellant 11	39·0
Propellant 12	26·0

Internal pressure at 20°C: approx. 30 psig (207 kPa).
Suitable container: tinplate.

Tinted hair sprays can be obtained by incorporating coloured aluminium powder or soluble dyes into the formula given in example 5. Colours and concentrations must be carefully selected to obtain the desired colour effect and also to avoid valve blockage in the case of solid colorants. Up to 4 per cent of solid material can normally be tolerated but it is advisable to include agitator pellets to assist dispersion.

Hair Dressings
Oil-based hair dressings can be formulated relatively easily. Products can range from simple solutions in mineral oil to more complex preparations containing, in addition, fatty esters, hair conditioning ingredients or aqueous alcohol.

Body Deodorants
Giacomo[31] has given various formulations. The bacteriostatic and bactericidal compounds discussed in Chapter 35 can be incorporated in aerosol formulations, for example deodorant colognes.

	(6) *per cent*
Perfume	0·7
Bactericide	0·3
Isopropyl myristate	1·0
Dipropylene glycol	3·0
Ethanol	65·0
Propellant 12	30·0

Internal pressure at 20°C: approx. 45 psig (310 kPa).
Suitable container: lacquered tinplate or lacquered aluminium.

Foams

The two-phase system can be used to produce transient coarse foams, using liquid propellants at low concentrations, particularly in product systems that are relatively viscous. Stable foams can be obtained using compressed gases that are soluble in the product phase. These systems may yet be shown to have application for toilet preparations.

Unchanged Products

Two-phase systems may also include certain unchanged products, such as pastes and creams dispensed by the use of an insoluble compressed gas such as nitrogen as the propellant. Large product retentions have been experienced, especially with viscous products. This particular difficulty may be overcome by employing a device which prevents contact between the liquefied propellant used and the product. This has been covered by a number of patents.[32–35]

The two-phase system using nitrogen as the propellant provides the simplest and cheapest method of dispensing products in an unchanged form. It is essential that the product is viscous enough to be extruded in a convenient form, yet sufficiently fluid to flow readily in the container. A rheopectic product can be ideal for this form of dispensing.

The most important product of this type to date is toothpaste, but many other products including liquid soaps, hand and hair creams, suntan creams and antiperspirant creams can be dispensed. Formulae can be adapted readily from standard conventional products.

THREE-PHASE SYSTEMS

In the treatment of two-phase systems it is assumed that the liquid phase is a completely homogeneous solution. However, many of today's products are based on emulsions, in accord with a trend towards water-based systems, for economic reasons, to avoid difficult solvents and partly for ease of formulation. If a product is in the form of a stable emulsion it is not difficult to consider it as a single phase in the context of a two-phase aerosol pack. But it is not always easy to preform stable emulsions to include liquid propellants and this leads to the concept of three-phase packs with two liquid phases which are emulsified, or mixed, by shaking at the time of use.

In a three-phase system the liquid propellant and the product no longer form a homogeneous liquid phase, as they do in the two-phase system, but are present as two distinct liquid phases. This system is used primarily for dispensing water-based formulations, including shaving creams and shampoos. The three phases of such a system are the aqueous phase, the non-aqueous liquid phase and the vapour phase—see Figure 40.6 a and b. The non-aqueous liquid phase, consisting largely or entirely of propellant, may be continuous, or it may be wholly or partly emulsified in the aqueous phase.

The three-phase system can be used to dispense space and surface sprays, foams and unchanged products.

The amount of propellant used in most three-phase systems is relatively small. Just sufficient of the chosen propellant is added to the aerosol to ensure the correct and complete discharge of the contents.

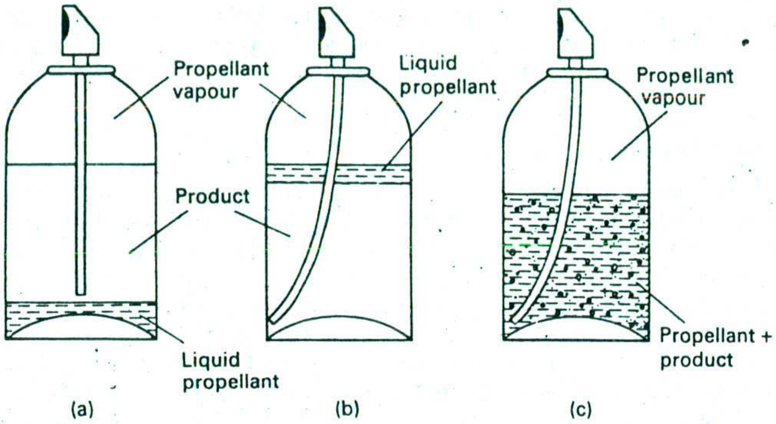

Figure 40.6 Three-phase aerosol systems

Another type of three-phase system is also possible in which a liquid phase, a solid phase and a vapour phase are present, as exemplified by antiperspirant and powder sprays—see Figure 40.6 c.

Liquid Sprays

Sprays can be obtained even though the liquid propellant and the liquid product are present as two distinct layers. Sprays can also be obtained by emulsifying the liquid product in a lipophilic external phase consisting entirely or partially, of liquefied propellant. These systems have been described in Du Pont publications[36] and also discussed by Root[37] and by Sanders.[38] Both space sprays and wet sprays can be obtained with this type of system which can be used for suntan sprays, room deodorants and others.

Sprays Containing Solids

Antiperspirants

The formulation of aerosol antiperspirants is discussed in detail in Chapter 10.

Suitable containers and valve specifications equal to the requirements of established formulations are readily available. A typical formula is given in example 7.

	(7) *per cent*
Aluminium chlorhydrate	4·0
Emollient Suspending agent Perfume	6·0
Propellant 11	35·0
Propellant 12	55·0

Internal pressure at 20°C: approx. 37 psig (255 kPa).
Suitable container: lacquered tinplate.

Powder Spray

Another variant of the three-phase system is the pressurized powder aerosol which gives a powder spray. The formulation of such sprays was discussed by Armstrong.[39] They consist of the product in particulate form constituting the solid phase, while the propellant forms both the liquid and the vapour phases. The liquid phase normally consists of the pure propellant, but sometimes it may also contain a small amount of dissolved lubricant to assist in the dispensing of the product by aiding the passage of the powder through the valve orifices. Sometimes the powder, for example talc, may have been treated with the lubricant. Because of the relatively low concentration of powder which can be incorporated (less than 20 per cent and more usually 10 per cent by weight) this system does not provide a very economic method for dispensing body powders. However, it can be used for dry shampoos[40] and talc and for dispensing antiseptic powders and other speciality products in powder form. Before use, the dispenser is shaken in order to ensure that the powder is uniformly dispersed throughout the liquid phase.

Caking and agglomeration have presented many problems in powder packs. In early sprays, clogging of valves occurred frequently, and dispensing was often poor. There is a limit to the amount of powder that can be incorporated in an aerosol pack, above which severe clogging of the valve and/or dispensing head is experienced, resulting in either intermittent discharge or complete failure. When the powder tends to aggregate, the addition of a suitable surface-active agent may be indicated.

The following formula illustrates this type of preparation.

	(8) *per cent*
Talc	9·0
Lubricant	0·5
Bactericide	0·1
Isopropyl myristate	0·2
Perfume	0·2
Propellant 11	45·0
Propellant 12	45·0

Pressure at 20°C: approx. 35 psig (241 kPa).
Suitable container: lacquered tinplate or lacquered aluminium.

In general, for powder sprays to be effective it is necessary to ensure that the solid particles are sufficiently small to pass screens of about 200 mesh and even finer, and exposure to moisture must be avoided in order to prevent the aggregation of powder particles. Furthermore, the product must be insoluble in the propellant to eliminate the possibility of crystal growth. For best results the densities of product and propellant should be similar.

Electrostatic Charges and Particle Sizes of Solids-containing Sprays

Electrostatic charge and particle size of sprayed solids are two issues of increasing importance which continue to occupy the thoughts and researches of the aerosol industry worldwide.

Electrostatic Charge. In anticipation of, and attendant upon, the virtual ban on chlorofluorocarbons in the USA, alternative propellants have been sought and found for all products, including such personal case products as antiperspirants and hair sprays. In general, hydrocarbons were adopted, with the exception of carbon dioxide in the field of men's hair sprays. Adoption of hydrocarbons for personal care products raised questions of flammability which were resolved by careful formulation and, more importantly, by choice of valve specification. However, one issue remains, that of electrostatic charge created when spraying powders, as with aerosol antiperspirants and talc sprays.

Such phenomena are well known scientifically in industry. The creation of such electrostatic charges on chlorofluorocarbon-propelled antiperspirants, produced in their thousands of millions since 1970, was never an issue. When hydrocarbon was substituted for chlorofluorocarbon as the propellant for powder sprays it was recognized that the electrostatic charge on the discharged contents might spark and cause an explosion.

There has been much activity in relation to this problem. In friendly and competitive vein, two groups, one in America[41] and one in Great Britain,[42] have sought to define and agree test methods. Codes of safe practice have been devised and are generally available. Individual companies[43] have been searching for quenching agents for incorporation into product formulations. Water is good, for example, but is unacceptable in antiperspirant formulations because of adverse effect on the product and problems of corrosion.

Particle Size. Again in relation to antiperspirants, particle size became an issue in America between the Food and Drug Administration and industry. Suppliers of active ingredients agreed to introduce new materials[44] with guaranteed particle size distributions so as to minimize the number of particles below 10 μm. Small particles, if inhaled and retained in the lungs, may constitute a health hazard.

The issue has become much wider and all types of sprayed aerosol products, and other spray forms, are now being examined. Laboratories are utilizing expensive equipment to measure particle size distributions for many products.[45–47] Many individual companies world-wide, as well as various trade associations, are looking at this whole question in order to determine the critical particle sizes, the levels of exposure to which consumers are subjected, and what real hazards are created.[48,49]

The trade associations—the British Aerosol Manufacturers Association (BAMA) in the United Kingdom, the Federation of European Aerosol Associations (FEA) in Europe, and the Chemical Specialties Manufacturers Association (CSMA) in the United States, and others—play a key role, through the collective and cooperative enterprises of committees and working parties, in recognizing such challenges and formulating work programmes to secure the well-being of the industry through the integrity of its products and production.[50]

Foams

Foams are normally obtained by the use of a three-phase rather than a two-phase system. Aerosol foams usually contain up to 15 per cent, usually 6–10 per cent, of liquefied propellant emulsified with an aqueous product in which a fairly high amount of surfactant is present. The container is shaken, the valve is actuated, and the emulsion which is forced up the dip tube emerges through the actuator. As soon as it reaches the atmosphere the dispersed propellant drops will immediately vaporize, and, in so doing, transform the product into a thick foam. Aerosols of this type are often fitted with a special foam head or spout. Such systems are discussed in some of the references quoted earlier in this chapter and in other Du Pont publications, and also under the appropriate product headings elsewhere in this book. The formulation of cosmetic foam preparations has been covered in a number of patents.[51–53]

Foam packs have been used to dispense shaving creams, shampoos and suntan foams.

While the constituents of the aqueous solution or the primary emulsion in the system, including the type and amount of surfactant, will undoubtedly influence the physical and functional properties of the foam, there is no doubt that the consistency of the foam, the rate of its formation and its stability will also be determined to a large extent by the type and the amount of propellant used, and hence the vapour pressure prevailing in the system. For a given concentrate, high vapour pressure propellants and high propellant charges tend to produce stiff, dry and elastic foams with poor wetting and spreading properties. Medium pressure propellants will produce a softer and wetter foam, while low pressure propellants and low propellant concentrations will give rise to soft, wet, less resilient, slowly forming foams. Interest in compressed gases for aerosol foams is developing.

When oil-in-water emulsion systems are to be dispensed as foams, the propellant vapour pressure will usually be between 20 and 50 psig (138–345 kPa) at 20°C and the propellant concentration will be 5–25 per cent of the total formulation, but usually towards the lower end of that range.

This system provides a very valuable method for applying a small quantity of cream to the skin and thus has found application also for hand creams, hand cleansers and suntan creams. It has application for liquid soaps,[54] shampoos and hair conditioners. However, the most important product in this class, until now, has been the aerosol shaving cream.

Shaving Creams

Aerosol shaving cream emerges from the nozzle of the container as a fully developed foam. For this purpose, propellants with vapour pressures of at least 25 psig (172 kPa) at 20°C are employed. A 40/60 mixture of propellants 12 and 114 at a level of 7–10 per cent may be used to produce a vapour pressure of 40 psig (276 kPa) at 20°C. With vapour pressures above 40 psig at 21°C the product will expand rapidly inside the valve actuator and emerge from the container in the form of a compact foam. The texture of the foam alters with increasing level of propellant, becoming more rigid and dry. It is interesting to note that butane foams are not flammable and have virtually replaced other propellants for these formulations.

The formula given in example 9 illustrates the composition of a shaving foam.

	(9) *per cent*
Stearic acid	5·9
Triethanolamine	3·1
Propylene glycol stearate	3·0
Lanolin	1·0
Glycerin	2·0
Lauric diethanolamide	2·0
Perfume	0·5
Water	82·5

92 parts packed with 8 parts of Butane 40.
Internal pressure at 20°C: approx. 40 psig (276 kPa).
Suitable container: lacquered tinplate or lacquered aluminium.

Shampoo

For aerosol shampoos a 'stream' foam, also referred to as a 'lazy' foam, is preferred. This is a soft type of foam which will spread easily but will not break down too readily. For this purpose, low pressure propellants with vapour pressures of 5–20 psig (34–138 kPa) are used, which will cause the product to emerge initially as a liquid or semi-liquid stream, which gradually expands to a foam. Normally about 40 per cent active matter is required. When using non-soap detergents, corrosion problems may be encountered.

The choice of propellants 12 and 114 in foam-type preparations is governed by their stability in the presence of water as well as by the fact that when used in combination they will produce any required vapour pressure. The foam pattern depends on the type of valve and actuator employed as well as on the propellant concentration, propellant type and the actual formulation. If the product used for producing foam is in the form of an emulsion, it should not be too viscous, otherwise it will not mix readily with the propellant and will subsequently dispense unevenly with accompanying spurting and propellant loss. In the case of an emulsion, foaming is also influenced by the type of emulsifying agent that is used in the preparation of the primary emulsion; those of the oil-in-water type are usually selected.

Water-based Systems

In a three-phase system comprising two immiscible liquid layers and containing a water-based product, the product forms one of the liquid layers, and the propellant forms the other as well as the vapour phase. Two possible situations exist, which are illustrated diagrammatically in Figure 40.6 a and b (page 826).

In (a) the propellant is heavier than the product and forms the lower liquid layer. This is generally the case with chlorofluorocarbon propellants. In (b) the propellant is lighter than the product (as in the case when the former is a hydrocarbon) and floats on top of the product. In either case (a) or (b) it is essential to shake the aerosol thoroughly immediately before use. In case (a) this is necessary to allow the two propellant phases to equilibriate so that the pressure in the head space is maintained; this occurs automatically with case (b). Also in case (a) the length of the dip tube requires careful adjustment to avoid dispensing neat liquid propellant which in turn causes product residue problems, through insufficient propellant.

The product is dispensed from the container when the valve is actuated. Special actuators are required to assist break-up of the coarse product particles, even though shaking, which causes entrainment of propellant in the product, materially helps in breaking up the product spray.

Care in the development of water-based products will resolve any problems which may arise with regard to the efficiency of the spray, compatibility of product and container in respect of corrosion, and correct balance of formulation and valve specification to control flammability when hydrocarbon propellants are used. As far as corrosion is concerned, with both chlorofluorocarbons and hydrocarbons full storage tests must be conducted with any development formulations. Mention may also be made of an article by Geary,[55] in which he discussed water–liquefied propellant–co-solvent systems designed to assist in the formulation of low cost water-based spray products.

PERSONAL CARE PRODUCTS WITH ALTERNATIVE PROPELLANTS

The reaction to the Rowland and Molina theory in 1974 imposed significant restriction on the use of chlorofluorocarbon propellants for aerosols in the USA[56] with echoes later in Sweden and Norway, while the EEC recommended a reduction of 30 per cent of the 1976 usage by the end of 1981.[57–59]

The aerosol industry in the USA, as well as in other countries, had already adopted hydrocarbon propellants for non-personal care products such as polishes, starches and paints, so that half of the aerosols produced were already dispensed by a flammable propellant, having an excellent safety record in production and use.[60] Carbon dioxide was used for de-icers, some surface insecticides and fire extinguishers.

The only personal care product, and a very important one in the USA, for which hydrocarbon was used almost exclusively was shaving cream. There were no hazards in this case because the hydrocarbon content was only 5–10 per cent, the product was water-based, it was not dispensed as a spray but as a foam, and this foam could not be ignited. The real problems in adapting to the use of hydrocarbons in the USA related to only two major personal products: antiperspirants, containing 90 per cent chlorofluorocarbon propellant, and hair sprays, which contained less chlorofluorocarbon propellant but a product concentrate rich in ethanol (hair sprays typically contained 50 per cent chlorofluorocarbon and 50 per cent of product based on ethanol).

In Europe, deo-colognes with 35 per cent propellant 12 and 65 per cent ethanol-based product became the third important personal care product requiring consideration of formulation revision with respect to propellant choice.

More recently, dimethyl ether has become of interest as an alternative propellant.[61,62]

Antiperspirants

Antiperspirants [63,64] are an important product category in the UK and the USA but not in continental Europe.

American antiperspirants, after a brief flirtation with hydrocarbon-propelled water-based emulsions, are now based on 80 per cent hydrocarbon and 20 per cent antiperspirant concentrate; such aerosols have also appeared in other markets. The difference in specific gravity—much lower for hydrocarbons than for chlorofluorocarbons—demands careful re-design of concentrate to achieve acceptable suspension characteristics and aesthetics and good spray performance. The absence of propellant 11 from the formulation contributes to the inferior performance of such aerosols.

In spite of the 80 per cent hydrocarbon content, choice of valve (vapour phase tap) and actuator ensures acceptable flammability characteristics when tested by Flame Extension Methods,[65,66] achieved largely by reduced discharge rate. Such aerosols, light in weight because of the reduced specific gravity of the propellant, feature a lower mass declaration on the label, last longer in the hands of the consumer and generally have a poor performance.

In the many countries which still permit the use of chlorofluorocarbons, many fillers and marketers, recognizing the lower costs of hydrocarbon, now use a blend of chlorofluorocarbons and hydrocarbons; they thus avoid the shortcomings mentioned above, while gaining in respect of reduced costs.

Hair Sprays

In the USA[67] basic hair spray formulations, using 25 per cent hydrocarbons and 75 per cent ethanol, are modified to accept (say) 8 per cent water or 10–15 per cent methylene chloride to provide solvency for the resins. Since these products consist of virtually 100 per cent flammables, choice of actuator and valve, even to include vapour phase taps,[68] is designed to produce good sprays[69] but with attenuated discharge rates[70] in order to control flame extension[71,72] and other characteristics. Performance of these products is generally good; they appear to have a longer pack life.

It should be noted that butane–water–alcohol systems will tolerate 8 per cent water in a single liquid phase. Care must be exercised to ensure correct choice of metal container specification in order to avoid corrosion problems.[73]

Carbon dioxide has been adopted in the USA as an alternative propellant for some men's hair sprays.

In Europe[74] the cost advantages of cheaper propellants are of course recognized, but their use is not so extensive because there are several important differences compared with America:

1. A total ban on chlorofluorocarbons has not been imposed.
2. Aerosols containing in excess of 45 per cent flammable materials incur labelling penalties.
3. In many countries ethanol is many times the price of chlorofluorocarbons.
4. The EEC Cosmetics Directive[75] restricts methylene chloride[76,77] contents to less than 35 per cent. The trend, however, is lower still, and in Germany an upper limit of 20 per cent has been imposed.

As for methylene chloride, so 1,1,1-trichloroethane seems to attract the attention of the legislative authorities and real concern is expressed in respect of future formulations, not only for hair sprays, over the possibility of greater restrictions being placed on propellant 11, methylene chloride and 1,1,1-trichloroethane.

One European basic formulation for a hair spray illustrates the approach to the above-mentioned regulations and restrictions:

	(10) *per cent*
Methylene chloride	35
Chlorofluorocarbon	20
Hydrocarbon Ethanol-based product concentrate	45

Hydrocarbon hair sprays similar to the American products are appearing in Europe in limited quantities. In Germany, for a time, specific chlorofluorocarbon hair spray formulations were modified to reduce the propellant content, substituting, say, 3 per cent by carbon dioxide. They were known as 'cocktails' or 'topped-up' systems.

Effective hair sprays based on nitrous oxide and propellant 11 have also been proposed.

Systems propelled by dimethyl ether can be devised to meet current European restrictions and regulations, as for hydrocarbon versions, and this relatively new propellant can accept up to 30 per cent water which also assists with respect to cost, solubility and flammability.

As for antiperspirants, so filler–marketers of chlorofluorocarbon hair sprays are able partially to substitute hydrocarbon in place of chlorofluorocarbons without change of container or valve specifications and without noticeable change of performance.

Deo-colognes

This European product,[78–80] also alcohol-based, suffers the same reformulation problems as hair sprays except that methylene chloride does not enter into the formulation equation. Topped-up (carbon dioxide–chlorofluorocarbon), hydrocarbon, hydrocarbon–water–alcohol, dimethyl ether–water and even straight carbon dioxide propellant systems have been tried, or are currently marketed while the availability of traditionally formulated products continues.

CORROSION IN AEROSOL CONTAINERS

In aerosol containers, as in other metallic containers, corrosion can result in product and/or pack damage. Since the system is under pressure and in the presence of a propellant, the corrosive action of the aerosol product may be accelerated and more severe than it would be if the same system were under atmospheric pressure. Sometimes it culminates in pack failure. Storage tests should take into account the nature of the product, its application and the market for which it is intended.

The study of container corrosion, apart from covering reactions between a product and its environment, also deals with suppression of corrosion by altering the characteristics of metals and their environment, for example by the use of protective lacquer films and the inclusion of corrosion inhibitors in the formulation, or by the modification of the latter.

While it is not proposed to give here a detailed exposition of corrosion theory, it is necessary to refer to the causes of internal corrosion in aerosol containers and to discusss ways of controlling them.

There are three main causes of internal corrosion in aerosols:

(i) Change of the propellant stability in the product environment.
(ii) Attack by the product.
(iii) Electrolytic interaction of dissimilar metals.

Propellant Influences on Corrosion

Some chlorofluorocarbons, although stable by themselves, show varying degrees of instability in contact with the constituents of the product (for example low alcohols) and the materials of the container (for example aluminium). The most stable among the common propellants is propellant 11, trichloromonofluoromethane. Its reaction with alcohol involving free radicals and leading to corrosion has been studied by many workers. It proceeds in the presence of trace amounts of air, but is inhibited if an excess of air is present. Sanders[81] proposed the following reaction chain, resulting in the formation of acetaldehyde, acetal, dichlorofluoromethane, ethyl chloride and symmetric tetrachlorodifluoroethane:

$$C_2H_5OH + CCl_3F \rightarrow CH_3CHO + HCl + CHCl_2F$$
$$CH_3CHO + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 + H_2O$$
$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$$
$$R\cdot + CCl_3F \rightarrow RCl + \cdot CCl_2F \text{ (free radical)}$$
$$2\ \cdot CCl_2F \rightarrow FCCl_2\text{—}Cl_2CF$$

R· represents an initiating amount of a free radical derived from a polyhalohydrocarbon by reaction with, for example, a metal.

Nitromethane has been regarded as an effective corrosion inhibitor in reactions involving free radicals.

In the presence of ethyl alcohol, hydrolysis of propellant 11 will occur at a rate depending on the ambient temperature. Its corrosive effect will be even more intense in the presence of large amounts of water.

The corrosion risk inherent in the use of a mixture of propellants 11 and 12 can be minimized by substituting for it a mixture of propellants 12 and 114, though it is by no means certain that these propellants will not react in a similar manner, even if at a slower rate.

In discussing corrosion due to propellants, mention must also be made of methylene chloride and 1,1,1-trichloroethane, both of which are used as auxiliary solvent–propellants or pressure depressants, and to replace the more expensive propellant 11.

Archer[82] correctly anticipated that reactions similar to those between propellant 11 and ethanol would take place between 1,1,1-trichloroethane and ethanol, and showed that appreciable corrosion of tin and iron did occur when metal strips were refluxed with such a mixture. The mixture causing maximum corrosion after 42 hours reflux was:

	per cent
1,1,1-trichloroethane	30
Ethanol	55
Water	15

In practice, the use of 1,1,1-trichloroethane, especially inhibited grades, together with anhydrous ethanol, should not present serious corrosion problems, but the introduction of even small quantities of water will increase the chances of corrosion and thorough testing will be necessary.

Product Influences on Corrosion

Corrosion as a result of direct chemical attack is comparatively rare in aluminium containers. It may result on contact with highly acid or alkaline solutions, and it can also occur in pressurized packs. Anhydrous alcohols (that is those containing less than 0·01 per cent of water) and also fatty acids are liable to attack aluminium. Aluminium containers are thus particularly prone to corrosion in the presence of ethanol or n-propanol, and products containing these alcohols should not be packed in internally unlacquered aluminium containers without adequate storage test experience.

Studies by Du Pont workers[83] on the corrosion of aluminum have indicated that the corrosive action of anhydrous ethanol is much more severe than that of 99 per cent ethanol, although it was pointed out that even with the latter it is still greater than the dispenser will tolerate. A number of reactions appear to be involved when corrosion by anhydrous ethanol occurs, chiefly alcoholysis of the propellant and attack of aluminium by hydrochloric acid produced during this reaction. According to Parmlee and Downing,[84] isopropanol appeared to be generally less corrosive than ethanol, but in many cases the difference was not great.

Products which contain isopropanol, even if they include propellant 11 (trichlorofluoromethane) as a constituent of the propellant mixture, can be packed in internally unlacquered containers, as long as the moisture content within the dispenser is not higher than 0·05 per cent.

Tin, like aluminium, will corrode in contact with solutions of high acidity or alkalinity. Corrosion in acid systems can further be aggravated by the presence of oxygen, following inadequate purging during injection filling, and has resulted, for example, in the discoloration of products by the dissolved tin; this has led to the lacquering of containers. However, Herzka and Pickthall[85] have pointed out that in lacquered containers the corrosive attack of acidic products 'will be concentrated at the pinholes which invariably occur in the lacquer film, and the perforation of the dispensers will be even more rapid than with internally plain dispensers'. These authors have also stated that corrosion of tinplate containers is not straightforward because of such effects as the inhibitory action on mild steel of dissolved tin and the reduction of the tin ion concentration by complex formation. A similar problem has been observed in aerosols containing alkaline products, such as shaving creams, again because of dissolution of the tin in the product, and production of a greyish discoloration. Although there is no danger of container perforation, the discoloration is undesirable and internal lacquering is again resorted to in order to overcome this defect.

Galvanic Action

In metal containers for aerosols more than one metal is often present, so that apart from a purely chemical attack by the product on the metal of the container, there are possibilities of galvanic corrosion, and several sites where it can occur. The two-piece aluminium container may constitute a greater corrosion risk than the one-piece monobloc container. Bimetallic interaction can occur in aluminium containers with tinplate bases or tinplate valve cups, especially with aggressive products and where any protective oxide or lacquer coating has been mechanically damaged. The tinplate base in a two-piece container will usually be cathodic to the aluminium body, but the polarity relationship will depend on the product characteristics. Cathodic metal is not at risk in respect of corrosion but forces metal which is more anodic to dissolve.

Even if all the container components are tinplate, two metals (tin and iron) are still present. The electrical properties of these may depend on the oxygen concentration. With some products when the oxygen concentration is low the tin may be anodic with respect to the iron, but at higher oxygen concentrations the tin may become cathodic and the iron anodic, and the latter becomes corroded. With other products the whole pattern may be reversed. The optimum level of air is a function of the product–package combination, and so vacuum purging of tinplate containers may be effective in reducing the potential corrosion of certain products.

Bimetallic corrosion can also be caused by traces of copper and by salts of heavy metals which must therefore be minimized. The adoption of blackplate and tin-free steel materials requires careful consideration.

Corrosion Inhibition and Prevention

In the preceding paragraphs réference has been made to the parts played by water, by oxygen and by the nature of the metal in contact with the product. Mention has also been made of the fact that some alcohols and some chlorofluorocarbons are more liable to attack containers than others. Attention should be paid, therefore, to control of the water content of the formulation, and to the efficient removal of oxygen from the head space of the aerosol either by vacuum or by purging with a compatible or an inert gas, where this is appropriate. Correct choice of alcohol and propellant will also minimize the possibility of corrosion.

Common corrosion inhibitors added in trace amounts to non-pressurized packs, such as neutral sodium silicate and ethanolamine phosphate, have not found general application in aerosols, because either they have not been found to be effective, or they are incompatible with the product or with its use. However, the use of specific corrosion inhibitors at empirically determined levels of addition has proved to be of enormous value, especially with water-based products.

Lacquers for Internal Protection

An important way of preventing corrosion is to separate the product and propellant from contact with the metal, and this is very frequently achieved by lacquering the interior of the container.

While unlacquered tinplate containers are liable to corrosive attack, particularly at the side seam, they seldom develop pinhole corrosion. Imperfections in a lacquer film, however, may give rise to this defect with acidic products, and perforation of container is likely to result more quickly than in unlacquered containers. Internally plain cans could also experience serious perforation problems if used for products that put steel at risk, for example some water-based products.

Cathodic metal is not at risk in respect of corrosion, but forces metal that is anodic to dissolve. Internally lacquered containers should preferably be used in systems in which the tin is cathodic to steel. In the circumstances of tin being anodic to steel, detinning results. Anodic attack is always more intense when a large cathodic area (tin) is in contact with a small anodic area (steel), a condition which occurs when flaws are present in the tin coating. As already explained, while tin is more noble than iron in the electrochemical series, in many solutions it is anodic to steel. Under those conditions only slow solution of tin will occur because of the small areas available for the equivalent cathodic reaction.

Internal lacquering is used in nearly all forms of metallic container where contact of the contents with the container would be deleterious in any way. This includes canned foods, and, in toiletries, collapsible tubes and aerosols.

Lacquers for metal aerosol containers must form a coherent film which is adherent, impervious, unaffected by the metal, unaffected by the product or propellant, and which does not affect the product. They must be tough but not brittle, having sufficient flexibility to withstand the manufacturing process because, while it would be possible to lacquer the partly made can and cover the base seam and the soldered side seam, it is impossible to lacquer the final seal when the valve assembly has been seamed on. The general practice is to lacquer the tinplate sheet before the three components for the tinplate can are fabricated, likewise for the aerosol cup. The can is formed in such a way that the portion of metal which is to form the side seam is left bare, to assist good welding (or soldering), after which it is later covered separately with a side stripe of lacquer.

Frequently a combination of a phenolic and an epoxy resin is used as a primer coating for the internal lacquering of containers. This may be followed by the application of two or even more coatings of an epoxy resin to prevent pinhole corrosion which, as pointed out above, is much more liable to produce perforation of the container than is the overall etching which occurs in unlacquered aerosols.

Phenolic lacquers are characterized by greater impermeability and chemical resistance than vinyl and epoxy resins, but their flexibility is rather low. Vinyl resins are tough, but have a poor adhesion to bare metal and are normally used over a base coat. Epoxy resins have good fabrication properties and have good adhesion to tinplate; because of this they are used as a base coat in many systems. An internal resin stripe is present in many containers to protect the product from discoloration or changes in odour or flavour following exposure to the metal at the side seam. Side stripes are applied, usually by spraying, immediately after the welding (soldering) operation, and the materials used for this purpose include oleoresins and vinyl resins.

The internal lacquering of aluminium containers is different from and not as easy as that of tinplate containers. While the latter are lacquered on the flat plate before fabrication, aluminium containers must be lacquered by spraying or flushing the finished container—a process which is rather expensive when dealing with monobloc containers. It is preferable, however, not to rely on the protection afforded by the lacquer coating, particularly where aluminium containers are concerned, but rather to use, as far as possible, non-corrosive formulations.

Anodizing

An alternative, or additional, method of protecting the internal surface of an aluminium container is the process known as anodizing, whereby the naturally occurring thin film of aluminium oxide is reinforced by a coherent, relatively thick (4–6 μm) and highly resistant layer of aluminium oxide. This film may be coloured to give, for example, a golden shine effect. Anodizing is expensive but gives a greatly increased corrosion resistance.

Electro-corrosivity[86,87]

Sophisticated and simple electrochemical methods for corrosion prediction have been devised over the years. Their basic purpose is to study the relationship between current and potential applied to all combinations of the basic metals occurring in a particular metal container construction, in the product environment for which the specific container is intended. Account is taken of the areas of metal exposed in the container as specified.

Significant advances in these techniques augur well for the aerosol industry in the 1980s, promising even greater confidence than has already been well established in making predictions about container behaviour after only 24 hours of study. Increasing experience facilitates the elimination of unsatisfactory specifications for the can, while screening out difficult product ingredients, for example unsatisfactory perfumes or surfactants.

Rapid exploration of alternative materials such as corrosion inhibitors ensures that only the product variations most likely to succeed in cans with favourable specifications are put on full storage tests.

In the event of complaint or failure, the services offered by electro-corrosivity facilities are invaluable in the inevitable investigation and especially when marketing continuity demands a temporarily substituted but compatible product.

Storage Tests

Full and adequate storage tests, whose design recognizes the aerosol product, its application and the market for which it is intended, are vital.[88,89] Failure to observe this simple rule is a recipe for ultimate disaster. Many filled aerosols should be stored, upright and inverted, with air levels which reflect production variations including lapses, both at ambient and elevated temperatures, for periods commensurate with the expected shelf life.

Experience should be developed to acquire confidence that results obtained after eight months at 35°–37°C, provided that the results at ambient temperatures are also favourable, are a reasonable guide to performance over two years in temperate climates. More rigorous testing is likely to be required for tropical regions.

ALTERNATIVE SYSTEMS

In the conventional aerosol, the product and propellant are in intimate association with each other. Early attempts were made, however, to develop methods which would enable these two components to be kept separate, particularly when they were found to be incompatible with each other and problems arose on storage and dispensing.

Piston Packs

Early developments led to the piston pack, in which a concentric plastic piston within the aerosol can was moved by the pressure of the propellant. An example of such a system was the American Can Company's container described earlier,[27] which prevented direct contact between the product and propellant and offered the possibility of packing products of relatively high viscosity into pressurized packs without the risk of cavitation and serious product residues. Problems have arisen, however, because of pressure equalization occurring on the two sides of the piston as a result, for example, of container deformation. Some products are still marketed in piston containers, for example pressurized cheese spread. The existence of piston packs has led to the development of different two-compartment packs, such as the Sepro-can, aimed at preventing the propellant from reaching the product.

The Sepro-can (Continental Can Company, USA)[90]

In early versions of this type of container the product was introduced into a plastic bag, which was then attached to the orifice of the container and sealed by means of a valve. The propellant was introduced through the bottom of the container, exerting pressure against the bag, so that when the valve was opened the product was dispensed. Further development of this system has led to the Sepro-can. This can contains a bellows-type plastic bag container held rigidly connected to the cone curl of the tinplate aerosol can. The product is filled through the bag aperture and the valve cup is then crimped into position, while the propellant is introduced through the concave bottom of the can by means of an orifice which is then plugged. Permeation through the bag that separates product and propellant may occur; nevertheless, this pack is successfully used in the USA, especially for a shave cream gel.

European Bag-in-can Systems[91]

Permeation through a plastic container was prevented in German developments. The bi-aerosol (Bi-aerosol Verpackungs GmbH, Germany) and the tri-aerosols, which operated on the bag-in-can principle, had thin aluminium foil in place of plastic bags, suspended within a standard aerosol can. The mode of operation was the same.

From Rhen AG, Presspack, and from Comes in Switzerland, commercially successful plastic bag systems are available. Recent innovation permits around-the-valve propellant injection, eliminating the need for propellant injection through an orifice in the can base with subsequent plugging with a rubber component. Claims for 98 per cent delivery are made for such systems, which have considerable potential application[92] in the packaging of food and pharmaceutical products and toothpastes within a wide range of viscosities, where the problem of product–propellant incompatibility has imposed severe limitations on the range of products which could be dispensed in this way. No doubt other applications in the toiletry field are possible to extend the range, and a claim has already been made for depilatories.

Compared with conventional systems, for which large amounts of propellant are used to bring about the dispensing, propellant contents are low for all bag-in-can and piston systems. While conventional valves and spray actuators may be used with these systems, the use of mechanical break-up actuators is necessary to achieve acceptable sprays where appropriate.

Tri-aerosol[91]

The principle of product–propellant separation embodied in the bi-aerosol was extended to the so-called tri-aerosol system which contained two internal containers. This permitted mixing of two products to activate them at the time of dispensing, for example mixing of an alkali base with stabilized hydrogen peroxide for bleaching hair. The outflow was controlled by a two-channel valve and the two products from the inner containers were then mixed in the required ratio, for example by valve nozzles of different diameters in the two-valve channels. The introduction of the tri-aerosol paved the way to co-dispensing, and marketing, of two-component and multiple-component products in a single pack.

Co-dispensing Valves

All major valve manufacturers have worked on the development of valves for co-dispensing. The early work was reviewed in *Aerosol Age* in 1968.[93,94]

The concept of co-dispensing, that is the dispensing of two or more products from a single aerosol container, was originated by Du Pont who secured two patents[95,96] disclosing valve modifications which would allow co-dispensing of two materials from a single aerosol container. Among the first valve manufacturers to obtain a licence under the Du Pont patent was the Clayton Corporation, USA, who developed the 'Clay-Twin' co-dispensing valve allowing the simultaneous dispensing of two different products in specified proportions through a common orifice. The introduction of co-dispensing valves has made it possible to dispense various products, including hot shaving creams and hair dye formulations.

Hot Shave Creams. To dispense a hot shave cream, the product incorporating a reducing agent is stored in a can, while hydrogen peroxide is placed in a laminated plastic bag. When the valve is actuated, the shaving cream and peroxide are dispensed and combined in a balanced proportion. This results in an exothermic reaction between hydrogen peroxide and the reducing agent (for example a mixture of potassium sulphite and potassium thiosulphate) and heating of the shaving cream. The proportions in which the two reactants are provided and combined are important. Serious problems, but different ones, develop with an excess of either component; insufficient peroxide gives only a lukewarm foam, whereas excess peroxide can lead to a liquid rather than a cream product. According to Du Pont, foam temperatures as high as 80°C have been produced with certain combinations of oxidizing and reducing agents.

The self-heating of shaving formulations based on the oxidation reduction principle has also been the subject of a US patent[97] issued to the Gillette Co. in which thiourea and substituted thiobarbituric acid derivatives were mentioned as reducing agents.

Co-dispensing Valves for Upright Containers. Early co-dispensing valves were designed to operate in the inverted position. However, OEL Inc., USA, also licensed under the Du Pont patent, developed a valve designed for use in the upright position.[90] In the package utilizing this valve, the oxidizing agent is enclosed in a polyethylene tube which snaps on the valve. The manufacturers have claimed that is is possible to fill their pack on standard equipment without the need for any special adaptations and that it is foolproof from failure in delivering the correct proportion of shaving creams and peroxide.

A co-dispensing valve system developed by the Valve Corporation of America consists of two distinct valve systems (referred to as a double compartment valve) and is operated with a single actuator.[94] The flow from each component is regulated by the size of the valve body and the depth of the slot in the stem. This valve system can be operated in either the upright or the inverted position.

The Precision Valve Corporation, USA, has fully researched co-dispensing valves operating in the upright position to the stage of final development.

Venturi Spraying

Reference has already been made to the fact that in systems such as the piston container, the Sepro-can and the Presspack system, where product and propellant are separated from each other by a plastic or metallic surface, it is not possible to effect satisfactory atomization. The attempts to combine separation of product and propellant with adequate atomization have led to the development of new systems in which the venturi principle has been utilized. The prototype of this system was a normal aerosol container which was filled with the liquid propellant and connected by means of a plastic bridge with a glass vessel holding the product to be sprayed. In connection with these developments, reference must be made to the Innovair system of Geigy, France, and the Preval Atomizer developed by the Precision Valve Corporation of America. In both these systems propellant and product are separated and only brought together at the moment of spraying. There is no need for the container holding the product to be pressure-resistant, which thus permits the use of materials other than metals.

The Innovair System (ITO). The Innovair system, originally known as ITO and used for insecticides and later air fresheners, was developed by Geigy S.A. of Switzerland and employed a blow-moulded non-pressurized container which held the product to be sprayed. The technical bulletin[98] dealing with this system described it as follows:

> An inner capsule contains the propellant which is maintained under pressure by the high-pressure valve. The latter is fixed in the spray head which comprises a push-button together with the venturi suction-and-spray micro-nozzle. A joint which forms the low-pressure valve controls the out-flow of the liquid and maintains the outer container at atmospheric pressure. When not in use the container is hermetically sealed, the high-pressure valve preventing the escape of the propellant, whilst the joint prevents passage of the liquid and its exposure to the atmosphere.
>
> When the three-way valve controlling the action of the pack is operated, the three exits will be opened, the propellant gas will pass through the spray cone, and will, when flowing through the venturi nozzle, produce a vacuum. The joint will connect the spray chamber of the venturi nozzle with the container holding the product, and will, when opening, compensate for the difference between atmospheric pressure and the vacuum formed in the container by the exit of the liquid. This will result in siphoning of the product from the outer container, and produce a spray. Air will simultaneously enter the container and replace the expelled product.

Several technical advantages were claimed for this system. The outer container which is no longer under pressure can be made from a number of plastic materials which in turn permits the use of containers in a variety of shapes and colours. It also provides chemical and corrosion resistance, thus overcoming many of the problems associated with the possible incompatibility in the pack of product and propellant encountered in tinplate and in aluminium containers. The system allows, for example, for the packing in aerosol containers of water-based products without the danger of producing extensive corrosion and can be used to dispense solutions, emulsions and suspensions. The unit can only be used in the upright position.

As with co-dispensing valves, maintaining the design balance for all production units, recognizing product tolerances, and all conditions and extremes of usage render an excess of one component over the other inevitable.

The Preval Sprayer[90]. The Preval system, developed by the Precision Valve Corporation, USA, also makes use of an aerosol cartridge consisting of a valve and a dip tube assembly, incorporating its own propellant chamber—again making it possible to eliminate the use of pressurized containers for the product and to use metal, glass or plastic. The difference between the Innovair and the Preval systems lies in the fact that in the former the product is supplied to the venturi nozzle around the propellant container, while in the Preval system the product passes through the propellant container into the venturi nozzle. Again, since the propellant joins the product at the point of discharge, the majority of compatibility problems hitherto encountered will not arise. Also, the use of the Preval cartridge will result in a reduction in the amount of propellant used, permitting the use of much lower propellant/product ratios. The Preval system is suitable, for example, for personal care products for salons, touch-up paints in garages, etc., as well as for do-it-yourself and hobby applications.

Aquasol

Aquasol[99–101] was introduced to the aerosol industry at the Chemical Specialties Manufacturers Association meeting in Chicago, in May 1977.

Hydrocarbon-propelled aqueous-based aerosol product systems, featuring vapour-phase tap valves, achieve remarkable results in terms of particle size and efficiencies when used for insecticidal and air freshener applications. Topically, however, such sprays are generally wet, while, in contrast, application for personal care products demands a dry spray.

For reasons of economy, water finds favour in aerosol products especially where the formulator—for example because of legislative restriction on the use of chlorofluorocarbons—has to consider alternative propellants such as hydrocarbon and seeks a ready modification of the flammability characteristics of the sprayed product. Aquasol was designed and offered to achieve dry sprays with such systems consisting—to quote an over-simplified example—of equal parts of hydrocarbon, water and ethanol, using a special valve and actuator button.

The established and simple principle is to introduce propellant gas into the liquid product stream by means of a vapour-phase tap, and this takes place in the housing or body of the valve. In the original Aquasol system the interaction of gas and liquid streams took place in the actuator button. A high velocity vortex of gas was arranged to strike the liquid stream tangentially just prior to release from the actuator button orifice. The violent swirl initiated production of very small uniform particles which resulted in a dry spray. For various design reasons this swirl feature—the interaction of the gas stream tangentially with the liquid stream—was later transferred to the base of the housing, thus permitting the use of simpler valves and a simpler design of actuator button.

Aquasol valve production, with designs at different levels of discharge rates, finds many applications for various types of product formulations beyond, but including, the hydrocarbon, water and ethanol systems originally proposed.

PROPELLANT-FREE DISPENSING PUMPS

The concept of a propellant-free dispensing system[102–109] is attractive for many reasons, chief among which are:

1. Simpler formulation of products.
2. Elimination of concern about propellant toxicity and flammability.
3. Simpler filling operations.
4. Absence of the need for a pressure-resistant container, permitting a wider choice of container material and pack shape.
5. The possibility (without the need to contain propellant material in a sturdy pressure-resistant container) of lighter and more compact packs, leading to improved portability and perhaps greater ease of handling and use.

6. The possibility of persuading the consumer that he is buying 'all product'.
7. Ready availability of refill packs.
8. Disposal the same as for any non-pressurized pack.

The challenge of producing a more efficient, less expensive propellant-free spraying system has existed and been pursued for many years. The objective has been to produce a system that is convenient, simple and safe to use, does not require special preparation before use, leaves no surplus product to be cleaned up and wasted after use and (of paramount importance) disperses the spray product over the application area so that the product is deposited in the required manner.

Hundreds of inventions exist and have been patented as propellant-free spraying devices but very few have been exploited on a commercial scale. The most important devices developed so far are the following.

The Plastic Squeeze Bottle

When the bottle is squeezed in the hand, the spray liquid rises through a dip tube to an injection-moulded spray plug where it is mixed with air entering the plug through vents near the top of the dip tube. The mixture then passes through a constriction in the plug, causing an increase in pressure sufficient to produce a spray break-up when the mixture leaves the plug. This system has been exploited over the years on products as diverse as hair lacquer, de-icer and nasal decongestants. A major disadvantage of the system is that when the pressure is relaxed on the bottle air is drawn through the dip tube and into the product, giving rise to product oxidation in certain cases.

The Rubber Ball Pump (Perfume Atomizer)

This system operates on the venturi principle. Air is blown from a rubber ball over the top of a tube which extends into the spray liquid. The liquid is drawn up the tube into the air-stream and diffused as a spray. This system requires a fairly vigorous pumping of the rubber ball and the rate of spray delivery is very slow. However, these pumps have been associated with the classic quality perfumes and still have a market value based on nostalgia.

The Elastomer Pressure Sprayer

In cases such as the 'Selvac' system, an elastomer bag, sealed to a dispensing valve and housed within an outer casing, is filled through the valve with product under pressure. The pressure energy is stored in the elastomer bag and provides the pressure for spraying. However, the spraying pressure is variable as the product evacuates. Aging and chemical attack may cause deterioration in the strength of the elastomer.

The Mechanical Finger Pump

The first consumer packaging use of mechanical sprayers was in 1946, when units made of PVC acetate were featured on certain household window cleaners. The wider availability of various plastics from 1962 enabled pump components to be moulded to the tolerances necessary to ensure efficient operation and to provide leakproof assemblies. Even then, the pumps that were available produced a coarse wet spray, which was suited to many household products but not at all satisfactory for products requiring fine atomization. The first 'fine-mist' pumps appeared in 1970 and performed well enough to secure by 1975 a significant share of the USA hair spray market. However, the 'first generation' of fine-mist pumps was vulnerable to consumer misuse: if the actuator was not pressed with a positive, firm finger-stroke, dribbling or streaming resulted instead of good break-up.

The difficulty of controlling the pressure at which the pump operates, and consequently of overcoming the problem of dribbling and streaming, is resolved in the 'second generation' of fine-mist pumps. Several excellent systems have been patented and they are usually described using terms such as 'pressure build-up', 'pre-compression' or 'constant pressure'. Characteristically, they feature complicated internal configurations and in manufacturing terms they are intricate, close-tolerance, multi-component assemblies. They have become an economic packaging entity only through the utilization of the most advanced moulding and assembly techniques and the development of sophisticated technical support to ensure consistent product quality and well-executed new product applications.

Particle size in a good spray pattern from a second-generation pump, it is claimed, can range from 10 to 40 μm. However, a careful product formulation is all-important to ensure good spray quality. A formulation with a high surface tension will give poor particle break-up, and high viscosity leads to streaming from the spray orifice. Materials with a broad chemical compatibility are used for the pump components. Pumps are designed essentially to spray solutions, and solids suspended in a liquid can be sprayed only if the particles are very fine and present in quantities of no more than about 10 per cent.

The great majority of conventional spray products can be packaged successfully in pump packs. There are also certain new product applications which have not been possible hitherto that can now be presented in a propellant-free natural spray, for example high concentration aluminium salt antiperspirant solutions and aromatic compounds susceptible to rapid loss of top-note; oxidation may be a problem.

Pumps available today to suit the various product applications fall into four major categories:

Regular sprayers	Sprayers with an output of about 1 ml and a medium-to-coarse spray.
Regular dispensers	Dispensers for lotions with the same output as regular sprayers, for example liquid soaps.
Fine mist sprayers	Sprayers with outputs ranging from 0·05 ml to 0·2 ml of a very fine spray.
Trigger sprayers	Sprayers with an output in excess of 1 ml and a horizontal rather than vertical actuation.

After 30 years of steady technical evolution of pumps the signs are that in the United States, and elsewhere, this particular type of propellant-free spray system—the pump—is achieving consumer acceptance.

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