DISPERSANTS

1. Introduction

Dispersants are compounds that are used to maintain particles suspended in a liquid medium, or assist in dispersing them. They are usually polymeric or oligomeric. Dispersants have many applications. They are used to disperse pigments in paints and inks, in water treatment, cement, builder assists, etc.

2. Function of Dispersants

Suspended particles attract each other due to van der Waals attractive forces. These forces increase very rapidly as the particles come closer to each other (see Fig. 1, curve **a**). This causes them to form clusters of particles, called flocculates. These flocculates (see Fig. 2) often detract from the properties of the system. Flocculation of pigments reduces gloss and color strength in paint systems. Flocculates of fouling or scale in cooling or heating water systems may precipitate and cause clogging or reduced heat conductivity. Flocculated particles in cement increase the viscosity and extra water is required to maintain sufficient workability. This in turn reduces the strength and increases the water

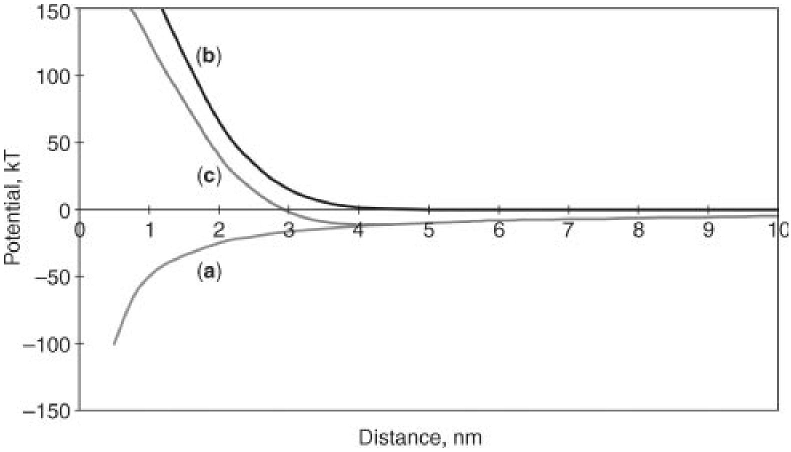

Fig. 1. **(a)** Potential energy curve of two particles as a function of their face-to-face distance. **(b)** The repulsion caused by a proper dispersant. **(c)** The sum of attraction and repulsion.

permeability of the final structure. Flocculated soil particles easily reprecipitate on laundry and reduce its whiteness.

Dispersants provide repulsion forces to counteract the particle–particle attraction, reducing or eliminating the flocculation or coagulation. Moreover, the viscosity of dispersions is reduced and a higher particle loading can be obtained. They adsorb onto particle surfaces, usually in amounts of 0.5–3 mg/m^2 of surface area, thus build a shell around them, which forms a barrier around

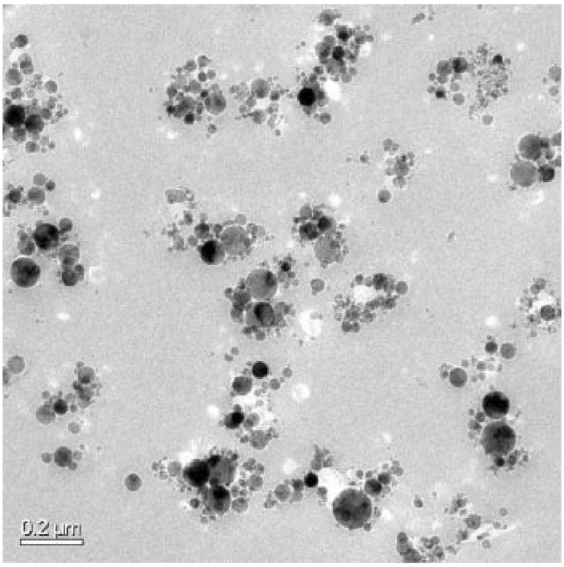

Fig. 2. Transmission electron microscopy (TEM) photo of flocculated TiO_2 particles. Photograph courtesy of Akzo Nobel.

Table 1. **Point of Zero Charge (Isoelectric Point) of Selected Inorganic Particles**

Particle	CAS Registry number	Isoelectric point pH
hydroxyapatite, $3[Ca_3(PO_4)_2]\ Ca(OH)_2$	[1306-06-5]	7
calcite, $CaCO_3$	[471-34-1]	9.5
hematite, Fe_2O_3 (dehydrated)	[1309-37-1]	5.2
(freshly formed in water)		8.0–8.7
rutile, TiO_2	[13463-67-7]	4.7
quartz, SiO_2	[14808-60-7]	2.2

the particle (see Fig. 1, curves **b** and **c**), that can stabilize the particles against flocculation in two ways: sterically and electrostatically. Dispersants acting only via electrostatic stabilization are rare, however. Very often, a combination of steric and electrostatic stabilization (usually called electrosteric stabilization) is used, and almost all of the dispersant described here work either via steric or via electrosteric stabilization.

2.1. Electrostatic Stabilization. Particles suspended in water usually have some surface charge. This charge is caused by either dissociation of ionic groups present in the particle material, by adsorption of ions (eg, H^+ or OH^- ions) from the aqueous phase or by adsorption of polymers with charged groups, like polyacrylic acid. This charge of course is pH dependent. At low pH values, the particle or ionic groups on the surface will be protonated, or OH^- ions will desorb, and the particle will be more positively or less negatively charged. Conversely, at high pH values the charge will become more negative or less positive. At a certain pH, depending on the particle's character, the net surface charge will be zero. This pH is called the isoelectric point (see Table 1).

If a particle has a positive or negative surface charge, a cloud of negative or positive counterions will collect around it (see Fig. 3). The charge on the particle and the charge of the counterions around it together form an electric double layer. When two particles approach each other, the clouds of counterions

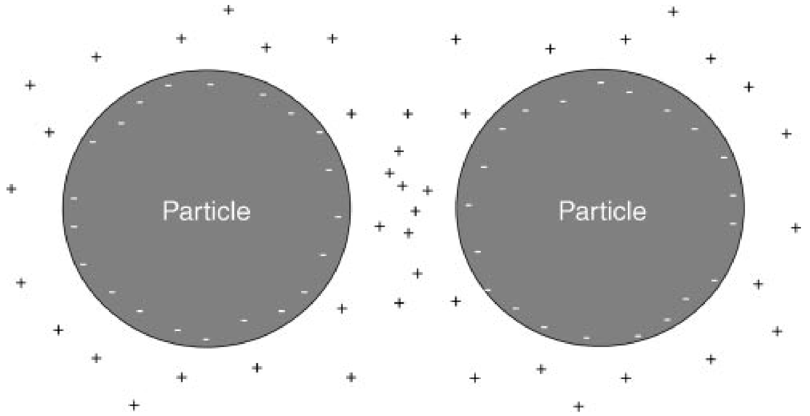

Fig. 3. Charged particles have a cloud of counterions around them.

of each particle start to overlap, which causes a repulsion between the two particles. This repulsion counteracts the van der Waals attractive forces of the particles and stabilizes the dispersion. The overall stability of a particle dispersion depends on the sum of the attractive and repulsive forces as a function of the distance separating the particles (see Fig. 1). DLVO theory, named after Derjaguin and Landau (1) and Verwey and Overbeek (2), encompasses van der Waals attraction and electrostatic repulsion between particles, but does not consider steric stabilization. The net energy between two particles at a given distance is the sum of the repulsive and attractive energies.

The counterions around the particle on one hand tend to diffuse away, but on the other hand, they are attracted by the charge on the particle surface. The balance between these two forces, diffusion and attraction, governs the average layer thickness of the counterions. When a salt is added to a dispersion, more ions are present in the bulk and the tendency of the counterions to diffuse away will decrease. Consequently, the double layer will shrink. Now particles can approach each other more closely before their shells begin to overlap and repulsion becomes effective, which may cause the dispersion to flocculate. The effect is even stronger if the salt contains ions with a high charge/mass ratio like Al^{3+}, as such ions are attracted more strongly by the charge on the particle.

It will be clear that no electrostatic repulsion will occur at the isoelectric point, where the net charge of the particles is zero. Consequently, particles can easily flocculate at pH values near the isoelectric point.

2.2. Steric Stabilization.

Considerable progress has been made in recent decades concerning the theory of calculating steric repulsive forces (3–7). When a polymer is adsorbed to a particle, it usually does not lie flat on the surface, but (in a good solvent) parts of the chains will protrude into the solvent or water. This solvated polymer builds a shell around the particle. When two particles approach each other their adsorbed polymer layers begin to interpenetrate (see Fig. 4).

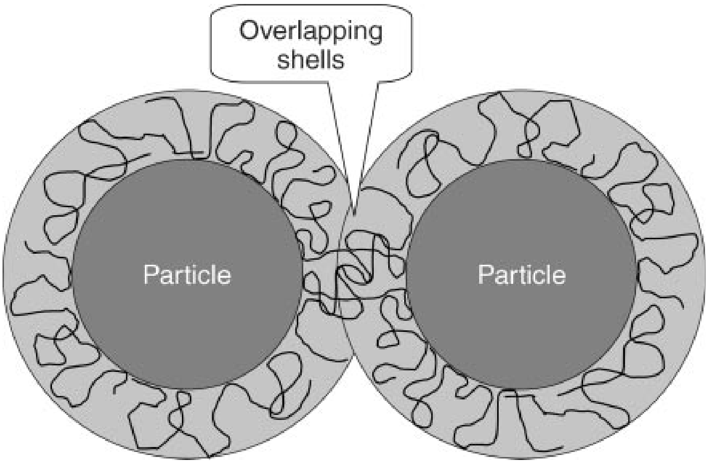

Fig. 4. Steric stabilization: adsorbed polymer builds a shell of solvated material around the particle. When two particles approach each other, their shells start to overlap.

In the overlapping part, the polymer concentration is higher and the degree of solvation is lower than in the rest of the shells. Moreover, due to the higher concentration, the polymer chains have a volume restriction, which causes a loss of entropy. As a result, the particles must separate to allow the chains more freedom of movement, while the solvent moves in to resolvate the polymer layer. As with electrostatic repulsion, an energy barrier is created. A common approximation used is that the strength of the energy barrier rises steeply at slightly less than the adsorbed layer thickness. In practice, a layer thickness of 5–10 nm is required to give sufficient stabilization against flocculation. The exact required layer thickness of course depends on the type and size of the particle to be stabilized, the medium in which it is dispersed, and the kind of polymer used to stabilize it. Advances have been made in directly measuring the forces between two surfaces using freshly cleaved mica surfaces mounted on supports (8), and silica spheres in place of the sharp tip of an atomic force microscopy probe (9). These measurements can be directly related to theoretical models of surface forces.

Some of the practical differences between sterically and electrostatically stabilized dispersions may be summarized as follows (10):

Steric stabilization	Electrostatic stabilization
insensitive to electrolyte	coagulation occurs with increased electrolyte concentration
effective in aqueous and nonaqueous media	more effective in aqueous media
effective at high and low concentrations	more effective at low concentrations
often reversible flocculation	coagulation often irreversible
good freeze–thaw stability	freezing often induces irreversible coagulation

3. Structure of Dispersants

Classical dispersants are simple linear or branched, random polymers. Trains of segments of these polymers adsorb to the particle surface, whereas other segments build loops or tails (see Fig. 5). These tails and loops can provide steric stabilization. In addition, in aqueous systems the polymer may have charged groups, both in the trains and in the tails and loops, providing electrosteric stabilization.

In traditional solvent-borne paint systems, the main binder was normally used as a dispersant. Here polar groups like carboxylic acid groups or hydroxyl groups cause adhesion to the pigment surface. Although the adhesion of such groups is only weak, due to the high molecular weight of the binders many of these groups are available and enough polymer adsorbs to the pigment surface to give sufficient stabilization. Classical dispersants such as linear (co)polymers of acrylic- or maleic acid were and still are used in many applications, like cooling

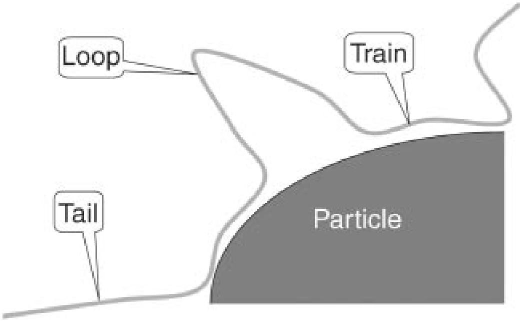

Fig. 5. Segments of a linear polymer adsorb onto a particle in trains, others build loops and tails.

and heating water, and reverse osmosis (see the section Recirculating Cooling Water).

For many applications, however, especially for paints and printing inks, the stabilizing properties of such dispersants became insufficient (see the section Paints and Inks). Novel synthetic techniques became available, which allowed more sophisticated dispersant structures than the random (co)polymers used so far. Several architectures have been devised for these so-called "superdispersants" or "hyperdispersants". All of them have anchoring sections, designed to adsorb onto a particle surface and stabilizing sections, which remain soluble in the surrounding medium (see Fig. 6).

Relatively simple AB structures, consisting of a soluble tail and only one, terminal, anchoring group have been prepared, both for solvent- and waterborne applications. Ring-opening polymerization of lactones results in a linear polymer with a terminal OH group, which can be converted to a phosphate group (11). The solubility of the polylactone tail is good in polar solvents, such as esters and ketones, whereas the phosphate group has a strong affinity for inorganic particles like titanium dioxide or iron oxide [see Fig. 7(**a**)]. Polycaprolactone, which is frequently used as the soluble tail, has the tendency to crystallize above a certain molecular weight. This crystallization limits its solubility in

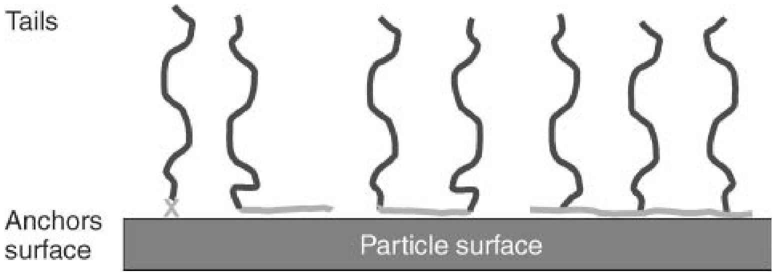

Fig. 6. Architectures used for modern "super-" or "hyperdispersants". Each consists of one or more soluble tails and an anchoring part that adheres to the particle surface. Left to right: AB dispersant, AB diblock, ABA triblock, comb.

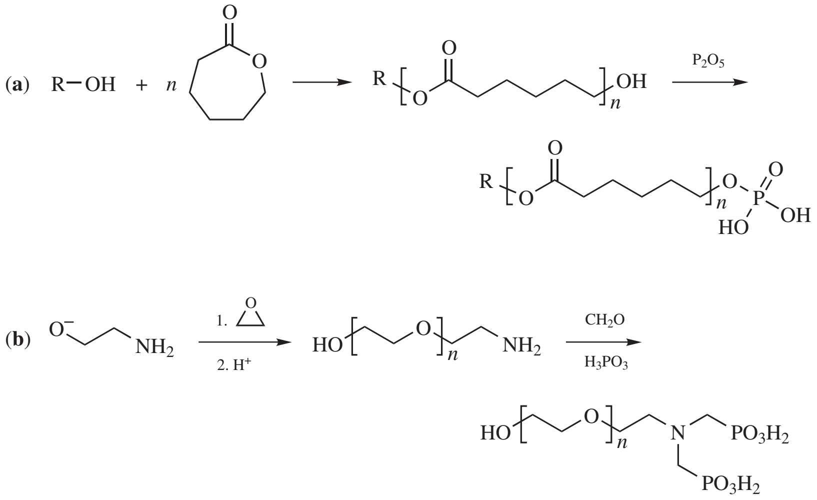

Fig. 7. Examples of the preparation of AB dispersants (**a**) is a solvent-borne dispersant, especially suited for inorganic particles and (**b**) is intended for water-borne applications.

many solvents and hampers application in some paint systems. Therefore, often mixtures of lactones, eg, caprolactone and valerolactone, are used for the preparation of the soluble polylactone tails.

Water-borne AB dispersants have been prepared by anionic polymerization of ethylene oxide using the aminoethanol anion as initiator, followed by a Mannich-Moedritzer reaction (12,13), see Figure 7(**b**). Here the amino (bismethylenephosphonic acid) group is a strong anchoring group for inorganic particles and the polyethylene oxide tail has good solubility in water. The material is very effective in lowering the viscosity of an aqueous slurry of calcium carbonate (14).

Alkyl phenol ethoxylates (APEs) are another class of AB dispersants. Here the alkyl phenol part acts as anchoring group, partly due to its insolubility in water, whereas the polyethylene oxide part acts as soluble tail. They are widely used as dispersants and surfactants, but are currently under pressure, especially in Europe, as their degradation products show estrogen-mimicking properties.

Simple AB dispersants have the disadvantage that they have only one anchoring group per molecule. This must be a very good anchoring group, as this one anchor must counteract the tendency of the soluble tail to diffuse away from the particle surface. Good anchoring is more easily obtained if a multianchor structure is used, eg, an AB-diblock structure (see Fig. 6). Here the soluble block A is connected to an anchoring block B, which contains several anchoring groups.

AB-diblock and ABA- or ABC- triblock structures have been prepared by sequential polymerization of vinyl monomers. Here, the middle block B is the anchoring section. Sequential anionic polymerization has been used to prepare dispersants consisting of an anchoring block of polyvinyl pyridine or polydimethylaminoethyl methacrylate and a polymethacrylic acid block, which is water-soluble under basic conditions (15,16) and provides electrosteric stabilization.

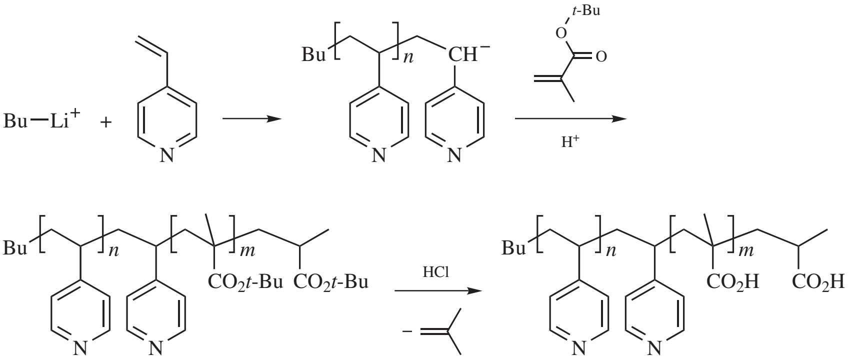

Fig. 8. Preparation of a water-soluble AB-diblock dispersant by sequential anionic polymerization of vinyl pyridine and *tert*-butyl methacrylate, followed by hydrolysis.

The latter block is prepared by hydrolysis of a poly-*tert*-butyl methacryate block (see Fig. 8).

Anionic polymerization is a procedure that is not easily performed on an industrial scale and is very much restricted in the choice of monomers. Therefore the use of AB diblocks and ABA triblocks as dispersants is relatively rare. Recently, new pseudo-living radical polymerization techniques like atom-transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT), and nitrogen-mediated polymerization (NMP) also called NOR-polymerization) have become available. This will allow much easier preparation of such compounds (17).

Reactions other than vinyl polymerization have been used to produce AB diblocks. Base-catalyzed polymerization of glyoxylic esters, using methoxy polyethylene glycol as starter, followed by hydrolysis of the ester groups resulted in an AB diblock with a polyethylene glycol (water-)soluble block and an anchoring block with many carboxylic acid groups. Reportedly, the material works well as dispersant for cement and pigments, as water-treating agent, and as detergent builder (18).

ABC-triblock dispersants have been prepared (19), in which the central part B is an anchoring block. The outer blocks A and C represent soluble sections, where one of them is water soluble and the other is soluble in organic solvents. In principle, such dispersants are suited for both solvent- and water-borne applications, as in solvent-borne systems the hydrophobic section dissolves and thus stabilizes the particles and the other section probably lies flat on the particle surface; in aqueous systems the situation is inverted. This allows the preparation of pigment pastes that can be used in both solvent- and water-borne paint systems.

Like AB-diblock and ABA-triblock polymers, comb dispersants are multianchor materials. They consist of a polymeric backbone, which anchors to the pigment surface, and soluble tails connected to it (see Fig. 6). They have been prepared in broadly two ways: by copolymerization of soluble-tail macromers (soluble tails, having a terminal polymerizable group), anchoring monomers and, if required, other monomers [see Fig. 9(**a**)], or by modification of existing backbones with soluble tails [Fig. 9(**b**)].

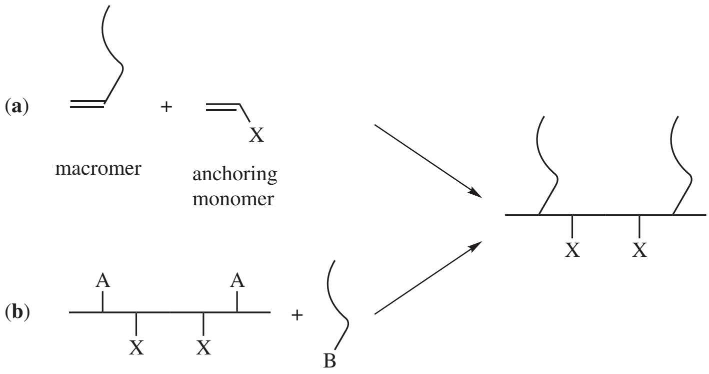

Fig. 9. Comb-shaped dispersants can be prepared in two ways: (**a**) by copolymerization of tail macromers, anchoring monomers and, if required, other monomers and (**b**) by modification of an existing, reactive backbone with tails. A reactive group A on the backbone reacts with a reactive group B at the end of the tail to give a chemical bond.

Numerous types of dispersants have been prepared in either of these ways, for solvent-borne, water-borne, or universal (ie, suited for solvent and water) applications. Acrylic tail macromers have been prepared by free-radical polymerization of methacrylate monomers in the presence of a Co(II) or Co(III) chelate chain-transfer agent. This results in a polymer with a terminal methacrylate functionality, which is copolymerized with monomers with urea- or imide functionality. The comb polymers have been used as pigment dispersants in solvent-borne systems (20). A similar procedure has been used to prepare water-soluble macromers, which were copolymerized with urea-functional monomers to give a dispersant used in water-borne ink jet inks (21). Methoxy polyethylene glycol (meth)acrylate has been copolymerized with (meth)acrylic acid, maleic anhydride, or vinyl phosphonic acid to give combs that produced dispersions of inorganic particles that were relatively insensitive to salts (22). Here the acid groups cause both anchoring to particle surfaces and electrostatic stabilization, whereas the water-soluble polyethylene glycol tails take care of steric stabilization.

In one application, both water- and solvent-soluble tails have been combined in one comb molecule. Hydrophobic acrylic macromers have been prepared first, which were then copolymerized with hydrophilic macromers like methoxy polyethylene glycol methacrylate and anchoring monomers like vinyl pyridine or vinyl imidazole. This resulted in dispersants that can be used both in aqueous and organic systems (23).

For the preparation of reactive backbones [Fig. 9(**b**)] a variety of monomers are available. Maleic anhydride and isocyanate-functional monomers like isocyanatoethyl methacrylate (IEMA) and dimethyl-*m*-isopropenylbenzyl isocyanate (mTMI) have been used to introduce reactivity with amino- or hydroxyl-terminated tails, the epoxy group of glycidyl methacrylate (GMA) is used to attach carboxylic-acid terminated tails to the backbone (see Fig. 10).

Water-borne comb dispersants for inorganic pigments have been prepared (24) by copolymerization of mTMI with butyl (meth)acrylate and styrene. The isocyanate groups on the backbone were then reacted with methoxy polyethylene

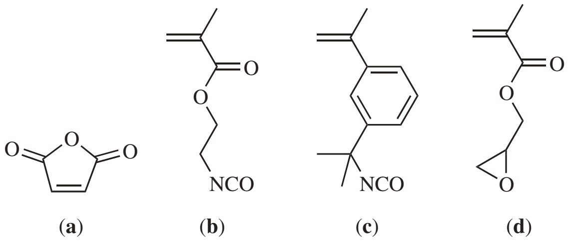

Fig. 10. Examples of frequently used monomers for the preparation of reactive backbones (**a**) maleic anhydride, (**b**) IEMA, (**c**) mTMI, and (**d**) GMA.

glycol as soluble tail and with hydroxyethyl ethylene urea to introduce cyclic urea anchoring groups (see Fig. 11) or with ethanolamine and polyphosphoric acid to introduce phosphate anchoring groups. By using the same chemistry, a series of comb polymers have been prepared, with different anchoring groups, such as hydroxy- (25), nitro- (26), amino- (27), hydrazide- (28), or ketimine groups (29). These polymers have been used as dispersants for inorganic and organic pigments in water-borne paints, and for the stabilization of aluminum flakes in water-borne basecoats.

A similar procedure has been used to prepare solvent-borne comb pigment dispersants by copolymerization of GMA and butyl methacrylate to form a reactive backbone. The epoxy groups were then reacted with a linear polyester with a terminal carboxylic acid group as soluble tails and with phthalimide as anchoring groups (30).

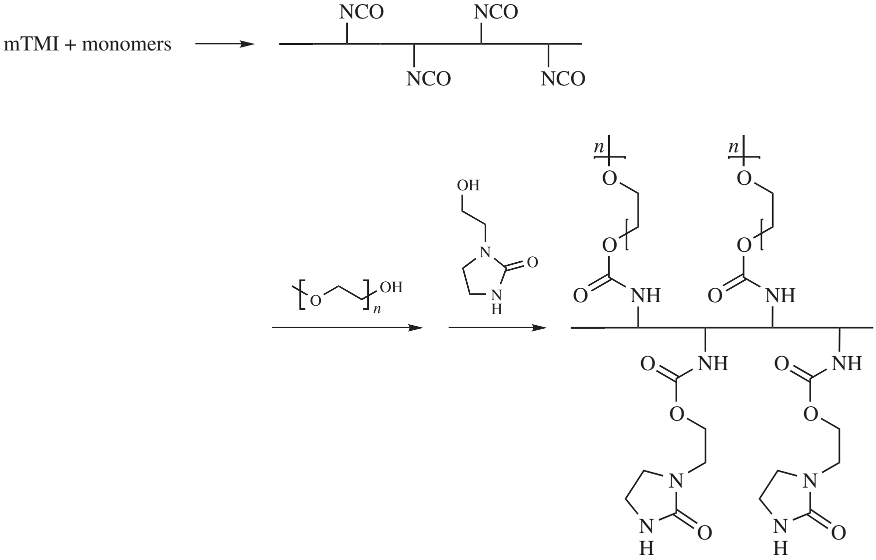

Fig. 11. Preparation of a comb-shaped dispersant. First a reactive backbone is produced by copolymerization of mTMI. This backbone is then modified with methoxy polyethylene glycol soluble teeth and with hydroxyethyl ethylene urea anchoring groups.

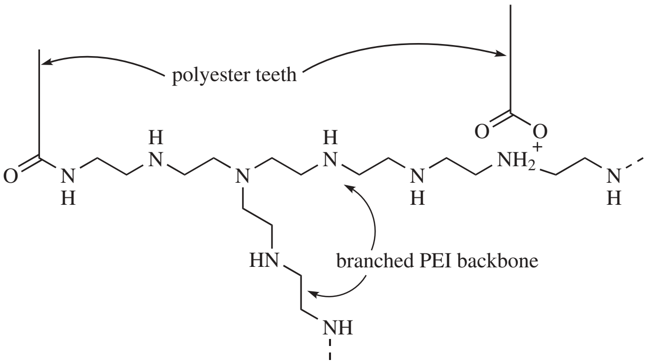

Fig. 12. Polyethylene imine (PEI) modified with polyesters with a terminal carboxylic acid group to give a dispersant for solvent-borne application. The polyester teeth can be connected through amide bonds (left) or through salt bonds.

Other backbones than vinyl polymers have also been used successfully to prepare comb dispersants. Polyethylene imine, which is well known for its adhesive properties, has been modified with polyester tails with a terminal carboxylic acid group, via amide bonds, salt bonds, or a combination of both (see Fig. 12). Polyhydroxystearic acid has been used as a soluble tail to prepare pigment dispersants for use in apolar systems like alkyd paints (31). Modification with the more polar polycaprolactone gave dispersants suited for more polar solvent-borne paint systems as used for car refinish or automotive OEM (32). Similar material has also been mentioned to disperse magnetic particles in organic solvents for the preparation of magnetic tapes and disks (33).

3.1. Anchoring Groups.

Adsorption is usually due to anchoring groups in the dispersants, which have specific interactions with the particle surface, eg, by hydrogen bonds, acid–base interactions, complex-, or ligand formation, overlapping orbitals, etc. Examples of frequently used anchoring groups are carboxylic-, phosphonic- (22,34) and phosphoric (11,35) acid, amines (36) or quaternary ammonium salts (37), and heterocycles like pyridine- or imidazole groups (38,39).

The specific character of these interactions makes it difficult to find universal anchoring groups, ie, anchoring groups that adsorb on every surface, which is particularly important in the paint industry, where a broad variety of pigments are used. A method for the selection of anchoring groups has been described (40,41). In this method, the adsorption of simple model compounds with anchoring groups is measured and from this process the free energy of adsorption ΔG is calculated. The parametric ΔG is a measure for the strength of anchoring. It allows the rapid screening of anchoring groups for a particle surface, without the need of preparing and testing a whole range of dispersants. An overview of adsorption energies for selected anchoring groups and pigments is given in Table 2.

Alternatively, anchoring can take place through nonspecific interactions. Many dispersants have segments that are insoluble in the solvent (or water) in which they are used. In this case, dispersants do not adsorb due to their affinity

Table 2. **Adsorption Energies for Model Compounds $C_2H_5{-}X$ to Pigments or Fillers**

Pigment or filler	Anchoring group X	ΔG_{ads} (kJ/mol)
transparent iron oxide[a]	carboxylic acid, pH 3	−17.3
	carboxylic acid, pH 9	−6.1
	sulfonic acid, pH 2	−10.2
	sulfonic acid, pH 7	−4.7
	sulfonic acid, pH 9	−2.8
	4-phenylol	−12.2
	amino acid, pH 7	−9.5
	amino acid, pH 9	−12.4
	amino	−7.1
	diethylamino	−0.3
	2-pyridyl	−10.2
	2-pyrazinyl	−13.3
	amide	−7.2
	acetyl, pH 7	−16.7
	acetyl, pH 9	−13.5
	methyl ester	−12.5
	$-OC_2H_4OC_2H_4OH$	−22.6
	$-OC_2H_4OH$, pH 7	−22.8
	$-OC_2H_4OH$, pH 9	−21.1
carbon black [b]	4-phenylol	−27.7
	2-pyridyl	−26.0
	4-pyridyl	−26.6
phthalocyanine [c]	2-pyridyl	−21.9
	4-pyridyl	−20.4
aluminum oxide [d]	4-phenylol	−10.7

[a] Sicotrans Red L2816 ex BASF.

[b] Heliogen Blue L7101F ex BASF.

[c] Farbruß 200 ex Degussa.

[d] ex Acros.

for the particles, but to their insoluble segment precipitating on the surface. Such dispersants are much more universal, ie, applicable to a broader range of particles, but their interaction with the particle is much weaker. If such a dispersion is diluted, the adsorption equilibrium shifts and dispersants may easily desorb, causing flocculation of the dispersion.

3.2. Soluble Tails. The soluble parts of a polymeric dispersant must extend into the solution, in order to contribute to the stabilization of the dispersion of particles. Whether they do so or lie flat or coiled on the particle surface depends on whether the continuous phase solvent is a good solvent (polymer–solvent interactions energetically favored) or a poor solvent (polymer–polymer and solvent–solvent interactions favored). The boundary condition between these two is referred to as the Θ (theta) condition or Θ solvent. At better than Θ conditions, the soluble chains are extended and will sterically repel chains absorbed on other particles and keep the particles apart. At worse than Θ conditions, the soluble chains tend to collapse and there is insufficient repulsion to prevent the interparticle attraction, leading to flocculation, or the particles may flocculate due to mutual attraction of the polymer layers (42).

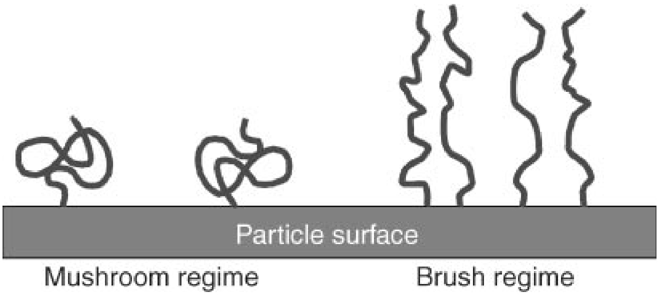

Fig. 13. Tails anchored to a particle surface form swollen coils of solvated polymer (mushroom regime), unless crowding forces them to stretch out (brush regime).

On the other hand, if the polymer–solvent interaction is so strong that it is greater than the anchoring energy, dispersant may be adsorbed only weakly. This finding can lead to the interparticle attraction dominating, so that, as the particles approach each other, the dispersant is desorbed and squeezed out of the space between them, allowing particles to flocculate or coagulate.

A tail anchored to a particle surface, just like a free tail, is loosely coiled up to a swollen sphere of solvated polymer (mushroom regime, see Fig. 13). The radius of this sphere is similar to the radius of gyration it would have in solution, which in turn depends on the molecular weight of the polymer and quality of the solvent (43,44). However, when many tails are connected to a surface, they force each other to stretch out (brush regime). It will be clear that the brush regime will give a better stabilization against flocculation than the mushroom regime. In the mushroom regime, some parts of the particle surface are uncovered and particles can still approach each other here. It has been found that the viscosity of a 20 wt.% slurry of calcium carbonate decreased rapidly with increasing level of dispersant until the level was reached where the surface was fully covered and the brush regime took over (14). Moreover, in the brush regime the soluble tails protrude further and thus build a thicker protective shell around the particle.

The solubility properties of a tail can easily be judged by testing whether it is possible to prepare clear solutions of it in a broad range of different solvents. For each solvent, the result of this test—soluble or insoluble—can then be mapped against its most relevant Hansen- or Hoy solubility parameters δ_H (the extent of hydrogen bonding) and δ_P (the polarity) (45). This has been done for complete dispersants (46) or for soluble tails only (41). It gives a very clear picture of the range of solvents and binders in which a given dispersant may be used successfully. An example of the solubility map for two frequently used soluble tails, polyhydroxystearic acid and polycaprolactone, is given in Figure 14. From the picture, it becomes clear that polyhydroxystearic acid tails are more suited for less polar systems like long-oil alkyds, whereas polycaprolactone tails are more useful in industrial and car-refinish paints with a higher polarity. The picture also shows that both tails can only be used in a relatively limited range of solvents. Dispersants having combinations of tails within one molecule have been used in order to broaden the solubility window (23,30).

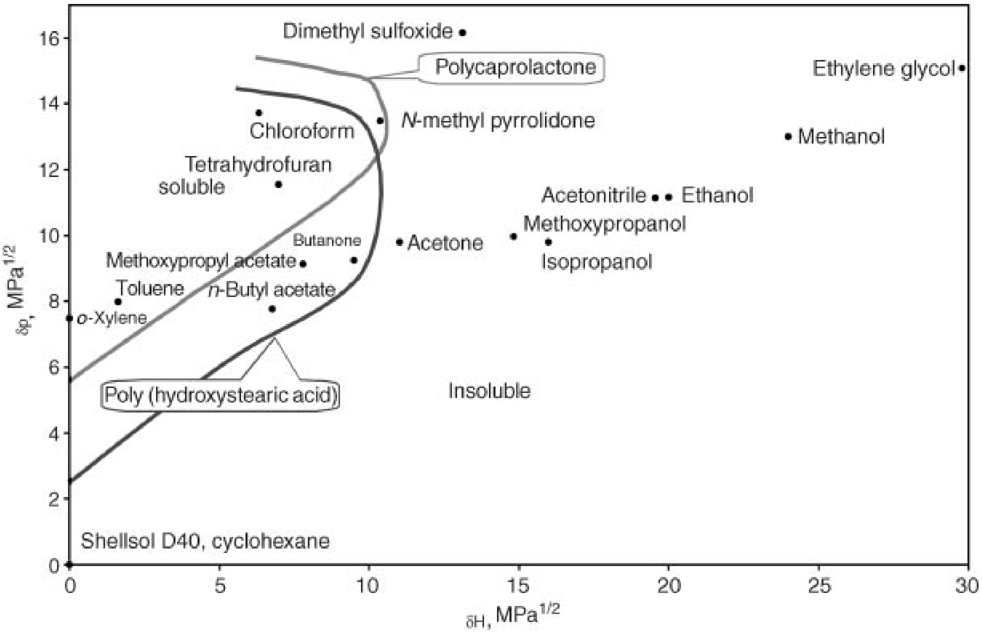

Fig. 14. Solubility plots of two frequently used dispersant tails, polyhydroxystearic acid and polycaprolactone. Solvents inside the curves are good solvents; those outside are bad.

As particles have been dispersed in very different media, in going from very apolar ones, like aliphatic hydrocarbons and mineral oil, to very polar ones like water, many different soluble tails have been used in dispersants. Polyisobutylene and polypropylene have been used as soluble tails in dispersants for very apolar systems like mineral oil (47). Polyhydroxystearic acid has been used in dispersants for apolar alkyd paints (31), whereas ethylene oxide/propylene oxide block- or copolymers (48) and polylactones (32) like polycaprolactone or polyvalerolactone have been used as tails in dispersants for more polar systems like flexographic inks or industrial and car-refinish paints. Copolymers are preferred both for the polyalkylene oxide and the polylactone tails, as the homopolymers (ie, polyethylene oxide and polycaprolactone) have a strong tendency to crystallize. Polyethylene oxide is used very frequently as a tail in water-borne dispersants (25). Polyacrylate tails have also been used frequently, in AB-diblocks, ABA- or ABC triblocks, or in comb polymers. By the appropriate choice of the monomers and the chain length, acrylic soluble tails can be tailored to match almost any continuous phase, from very apolar, using monomers like lauryl methacrylate (23), to aqueous systems using (meth)acrylic acid homo- or copolymers (21).

There is a certain optimum for the molecular weight of soluble tails. Of course, longer tails will build a thicker protective shell and thus give more protection against flocculation. However, the protective shell adds to the hydrodynamic volume of the particle and the latter governs the relative viscosity of the pigment dispersion. The viscosity of a particle dispersion goes to infinity when particles plus protective shells have their closest packing (63% by volume for identical spheres in random close packing, 74% for hexagonal packing) and the more shell there is, the less is left for the particles themselves. This finding is especially true for small particles, where a shell of say 10 nm thickness constitutes a large part of the total of particle plus shell. In practice, for water-borne systems good results have been obtained with polyethylene oxide tails with a molecular weight of 1000–2000. If such a tail would be fully stretched, it would have a length of 7–13 nm.

4. Comparisons With Other Materials

4.1. Surfactants vs Dispersants. Surface-active agents or surfactants (qv) are occasionally used as dispersants but are mainly used in other applications. Surfactants are used in a whole range of two-phase interface systems: water-in-oil and oil-in-water emulsions, change the surface tension at the air–water interface, improve wetting at the solid-in-water interface. Dispersants are only used to stabilize particles either in water or in solvents. As indicated, surfactants are sometimes used for this purpose either because the dispersions are not stable enough or the surfactants are too expensive. Consequently, the terms dispersant and surfactant are frequently confused. However, there are several important differences between the two classes of materials. For example, surfactants, which are small molecules containing both a hydrophilic and a hydrophobic portion, are defined by the nature of the molecule. Surfactants tend to orient at the air–water interface, oil–water interface, or sometimes at a liquid–solid interface depending on the length of the hydrophobic portion and the nature of the hydrophilic part (anionic, cationic, or nonionic). In contrast, dispersants, which tend to be larger polymeric molecules, are defined more by their use, which is to disperse a solid in a liquid. Surfactants adsorb at surfaces, preferring to be out of the water phase. Dispersants mostly adsorb by means of chemisorption or electron transfer, using specific anchoring groups. As an example, most dispersants will not adsorb at latex surfaces, in contrast to surfactants, which do. Although there are some dispersants that have significant surfactant-like properties, a quantitative way to distinguish the two classes is by measuring their surface tension in water. A 0.02% by weight solution of a surfactant produces a surface tension of <40 mN/m (= dyn/cm), whereas in a dispersant solution it will generally be above that number.

4.2. Chelants and Precipitation Inhibitors vs Dispersants. Dispersants can inhibit crystal growth, but chelants, such as ethylenediaminetetraacetic acid [60-00-4] (EDTA), and pure precipitation inhibitors such as nitrilotris-(methylene)trisphosphonic acid [6419-19-8], commonly known as amino trismethylene phosphonic acid (ATMP), can be more effective under certain circumstances. Chelants can prevent scale by forming stoichiomctric ring structures with polyvalent cations (such as calcium) to prevent interaction with anions (such as carbonate). Chelants interact stoichiometrically with polyvalent cations, in preference to adsorbing on surfaces. Pure crystal growth inhibitors such as ATMP adsorb nearly completely to surfaces, and thus do not provide enough residual negative charge for Coulombic particle repulsion and dispersion.

Table 3. **Comparison of Performance of Materials by Functional Class**

Material	Function	Typical dosage ppm	Ratio of cation to material[a]	Oil emulsification	Kaolin dispersing	$CaCO_3$ growth inhibition (%)
EDTA	chelant	20–100	1:1	poor	poor	100
ATMP	crystal growth inhibitor	5–10	10^2–10^4:1	poor	poor	90–100
polycarboxylic acid[b]	dispersant	5–1000+	10 – > 10^6:1	poor–fair	very good	80–90
anionic surfactant	surface-active agent	100	na	very good	fair–poor	<30
anionic polyacrylamide[c]	flocculant	5–100	na	poor	very poor	<10

[a] Not available = na.

[b] 2000 molecular weight.

[c] 5,000,000 molecular weight.

4.3. Flocculants vs Dispersants. In direct contrast to dispersants, flocculants or coagulants are used to aggregate fine particles or liquid droplets in aqueous media to improve separation of the two components. Flocculants function by charge neutralization, double-layer compression, particle bridging, or by forming large nets that engulf masses of particles (sweep flocculation). Dispersants normally function by charge repulsion, steric repulsion, or both. Some polymeric flocculants can be chemically similar to dispersants, differing only in molecular weight and dosage level used. However, dispersants are normally anionic materials of lower molecular weight and higher charge density than polymeric flocculants (see FLOCCULATING AGENTS).

In summary, dispersants are effective for particle dispersion and crystal-growth inhibition, but do not normally have surface-active properties such as oil emulsification. Chelants and antiprecipitants frequently inhibit crystal growth better than dispersants, but are ineffective for particle dispersion. Flocculants are effective for aggregating particles, the opposite function of a dispersant.

An illustration of the key performance differences among these different classes is given in Table 3.

5. Uses

5.1. Recirculating Cooling Water. Water used to cool plant processes and buildings contains contaminants that can accelerate corrosion of metal surfaces and leave scale or particle deposits on pipes and heat-transfer surfaces. To prevent corrosion and scale, cooling water treatment formulations contain corrosion inhibitors, biocides, phosphonates, and dispersants. Dispersants aid in the prevention of inorganic fouling (silt, iron oxide), scaling (calcium carbonate, calcium sulfate), and corrosion. The dispersant minimizes settling of inorganic foulants by adsorbing on particles to increase their mutual repulsion (49).

Dispersants prevent scale by adsorbing on active sites on growing crystals, ideally minimizing their particle size to less than the wavelength of visible light, making them invisible to the unaided eye. Small particles settle out on pipes and surfaces less easily, following Stokes law. In addition, the relatively large surface area of these particles favors their redissolution. Dispersants also restrict the particle size of corrosion-inhibiting agents such as calcium phosphonate and zinc. In alkaline cooling water treatment, corrosion inhibitors form films at high pH cathode areas on a corroding metal surface. By helping to minimize the particle size of these corrosion inhibitors in the bulk water, dispersants enable the inhibitors to precipitate preferentially at cathode surfaces as a thin film of closely packed particles in the form of a hydroxide salt or complex (50). Specialty dispersants have been developed to prevent specific inorganic scales and particles from fouling cooling water surfaces. For example, calcium phosphate and iron are controlled with copolymers of acrylic acid-nonionic monomers (51,52), acrylic acid-sulfonate monomers (53), or acrylic acid-sulfonate-nonionic terpolymers (54). Calcium carbonate is controlled with poly(maleic acid) (55) and organic phosphonates. Dispersants designed to control silica and magnesium silicate (56–58) have also been introduced.

5.2. Boiler Water. Dispersants are used to prevent scale buildup on the boiler tubes and drums of boilers that operate at pressures $\lesssim$10.3 MPa (1500 psig). Above that pressure, the temperature is too high for most dispersants and they break down into less effective fragments (59). Boiler water treatments using dispersants generally fall into three categories: precipitation programs, where water hardness ions are preferentially precipitated as calcium carbonate or hydroxyapatite (calcium phosphate hydroxide) and are dispersed in the bulk water rather than at the metal surface; dispersant and chelant combinations (60), where the dispersant is used to control precipitates formed from excess hardness leakage from water pretreatment; and dispersant only (61–63) or dispersant plus sequestrant (64), where dispersants bind hardness ions to prevent precipitation and scaling with polyvalent anions. A significant fouling problem in boilers is iron, which can be controlled with specialty dispersants (65) that are not deactivated by ferrous(ic) ions.

5.3. Geothermal Fluids. Geothermal fluids are used to provide energy for power generation and home heating. When heat or steam is extracted from geothermal fluids, the fluid (water) has a greater tendency to deposit scale. Scaling causes pipes, wells, and drains to become blocked, reinjection wells to become less receptive to waste fluid, loss of heat energy, and environmental problems (66–68). In most cases, the scale is comprised of either silica or calcium carbonate. Dispersants are used to change the surface of the precipitates formed so that they no longer adhere to the other surfaces. It is likely that the dispersants minimize scaling from geothermal fluids by modifying crystals and by increasing Coulombic repulsion of the particles formed.

5.4. Seawater Distillation. The principal thermal processes used to recover drinking water from seawater include multistage flash distillation, multieffect distillation, and vapor compression distillation. In these processes, seawater is heated, and the relatively pure distillate is collected. Scale deposits, usually calcium carbonate, magnesium hydroxide, or calcium sulfate, lessen efficiency of these units. Dispersants such as poly(maleic acid) (69,70) inhibit scale formation, or at least modify it to form an easily removed powder, thus maintaining cleaner, more efficient heat-transfer surfaces.

5.5. Reverse Osmosis. In contrast to distillation, reverse osmosis (qv) (RO) uses hydraulic pressure as its energy source to purify water. In RO, a fraction of the water content of seawater or brackish water is driven under pressure through a semipermeable membrane. The impure water, flowing past the membrane in several stages, becomes progressively more concentrated. The membrane, which is usually cellulose acetate or polyamide, can become fouled with silt, calcium carbonate, iron, or silica. Dispersants are used to minimize fouling and decrease the frequency of flushing or cleaning (71,72). Dispersants are also used in proprietary membrane cleaning agents (72). Since the water quality, (measured by the amount of salt passage through the membrane) from RO treatment can be traded off for increased flux (volume), this methd is often combined with multistage flash distillation to produce drinking water of acceptable quality and high volume (73). To conform to regulations for the production of drinking water by RO, specially produced grades of poly(acrylic acid) (74) or other dispersants must be used.

5.6. Sugar Processing. Dispersants are used in the production of cane and beet sugar to increase the time between evaporator clean outs. Typical scale encountered include calcium sulfate, calcium oxalate, calcium carbonate, and silica. Dispersants are fed at various points in the process to prevent scale buildup, which would interfere with efficient heating of the vessels. Only certain dispersants, conforming to food additive regulations, can be used, since a small amount of the dispersant may be adsorbed on the sugar crystals.

5.7. Oilfield. Scales can plug a producing well, requiring expensive remediation or even requiring a new well to be drilled. Scale also forms on topside equipment and piping, which is usually less difficult to handle. One primary cause of scale formation is the mixing of incompatible waters from either two different aquifers or, in the case of off-shore drilling, from the mixing of seawater with formation water (75,76). The problem is aggravated by the release of gas pressure, eg, carbon dioxide, at the wellbore, which raises the pH and increases the risk of calcium carbonate formation. The most frequently encountered scales are calcium carbonate, and barium, strontium, and calcium sulfate. Polymeric dispersants (77) and organic phosphonates are most often used to prevent oilfield scaling by delaying precipitation and preventing scale adherence on pipes and surface equipment. Scale inhibitors are normally injected (squeezed) into the producing well periodically at high dosages to force adsorption onto formation surfaces near the wellhead (78,79). The inhibitor then slowly desorbs and is produced with the oil and formation water at low levels over time, preventing scale formation. This process is repeated when the phosphonate or polymeric dispersant falls below effective levels.

5.8. Drilling Muds. Aqueous drilling muds normally consist of bentonite clay, weighting agents such as barite, dispersants such as lignite, lignosulfonate, and various polymers, and fluid loss agents. Bentonite clay is used to modify mud rheology so that drilled cuttings can be carried to the surface, and to help seal off the drilled hole so that fluid does not easily penetrate into the surrounding formation causing washout or hole collapse. Bentonite clay consists of flat plate particles with negatively charged faces and positively charged edges, which attract each other to form an open card-house structure that does not have good wall-sealing and rheological properties. A dispersant neutralizes the positive edge charges of bentonite particles, allowing them to lay flat against the sides of the drilled hole to minimize water intrusion into the formation. Weighting agents, for increasing the density of the mud, must also be dispersed. Seawater muds (offshore drilling) and gypsum muds require specialty dispersants that have higher divalent cation tolerance than dispersants used in freshwater muds. Chrome lignosulfonate has been the preferred dispersant for these wells, but is now being replaced by polymeric acrylic dispersants (80–82) because of the harmful effects of chromium on the environment.

5.9. Cement. Although water is needed in the hydration reactions of cement (qv), excess water added for workability of the concrete and mortar creates voids that decrease strength and increase water permeability. Dispersants are used as plasticizers in cements to cut water demand by up to 40% and decrease void volume. This results in much higher early strength and less water permeability in the concrete (83–85). Superplasticizers function by adsorbing on the surface of alite (tricalcium silicate, the principal constituent of Portland cement). This adsorption increases the charge repulsion of the particles, allowing less water to be used while maintaining low slurry viscosity (increased workability). Reportedly, superplasticizers retard the hydration of alite by limiting its interaction with water molecules and minimizing the dissolution of calcium ions that normally further react as the cement cures (86). The two main classes of superplasticizers are melamine–formaldehyde condensates and naphthalene-sulfonate condensates. Newer superplasticizers derived from acrylic acid-based polymers require only ~30% of the dosages of earlier types (87–90).

5.10. Paints and Inks. Typically, a paint (qv) contains pigments (qv) to provide color and hiding or coverage, polymeric binders to hold the coating onto the surface, dispersants, thickeners, flow and leveling aids, defoamers, and biocides. As they are customarily supplied, pigments are powders consisting of agglomerates of individual pigment particles. Pigments must be dispersed in the liquid medium and stabilized at their primary particle size to provide maximum hiding and film properties (91,92). The dispersion process involves three steps. The first step involves wetting the pigment particles, which is done by the dispersant or with an auxiliary surfactant, if the dispersant is not an efficient wetting agent. The second step is to break down agglomerates, requiring energy supplied by a high-speed disperser, a bead mill, or other grinding equipment. The resulting dispersion must then be stabilized, which is the primary function of the dispersant. This requires maintaining the pigment particles in their dispersed state during the manufacture, storage, application, and drying of the paint. Pigments are usually the most expensive raw material in paints and can only show their full color strength if they are well dispersed. Therefore the use of an optimal dispersant can easily contribute to obtaining the required color from the minimum amount of pigment and thus help to minimize raw-material costs. Moreover, a good dispersant can assist in the grinding process and thus help reducing process and energy costs.

A special requirement in the stabilization of pigments in paints arises from the fact that nearly always a combination of different pigments is used, to obtain the required color. Very often, differently colored paints or color concentrates are mixed at the point of sale or at the point of application. Since not every pigment can be stabilized with the same dispersant, in many cases different dispersants have to be used for different pigments. This can lead to problems when certain combinations of pigments are mixed, eg, due to exchange of dispersants between pigments, due to surface charges of different signs causing mutual attraction of pigments (coflocculation), etc. Although much progress has been made in the prediction of color properties of mixtures, experimental verification of the final color is still required.

In traditional solvent-borne paints, the pigment was usually dispersed using the main binder. Due to the high molecular weight of this material, enough adsorption took place to build a stabilizing shell of sufficient thickness. However, newer paints with a lower level of organic solvents required binders with a lower molecular weight, and stabilization of the pigment by the main binder was no longer good enough. Moreover, as high-solids paints contain less solvent, they have a higher pigment load than traditional solvent-borne paints. This again requires the use of good pigment dispersants in order to minimize particle–particle interactions and keep the viscosity as low as possible. A broad range of solvent-borne pigment dispersants have been developed over the years (93), both by specialized suppliers for commercial uses and by paint manufacturers for internal use. Soluble tails going from very apolar, eg, polyhydroxystearic acid, to polar, like polylactones and ethylene oxide/propylene oxide copolymers have been used, to cover the whole range of solvent-borne paints from long-oil alkyds to industrial and car-refinish paints.

In water-borne latex paints, normally linear polymeric acrylic dispersants are used to obtain a stable pigment dispersion, although polyphosphates and other low cost dispersants are sometimes used in grinding the initial dispersion. There are three principal types of polymeric dispersants, each having a balance of advantages and disadvantages (94). Dispersants based on poly(carboxylic acid) are usually the cheapest and the most efficient in producing the initial dispersion, but ordinarily do not produce high gloss in latex paints. Copolymers of an acid and a hydrophilic comonomer are less efficient than the polyacids, but frequently provide much higher gloss, and have good compatibility with various thickeners used in paints. Copolymers of an acid and a hydrophobic comonomer are also less efficient than the polyacids, but, again provide high gloss. The hydrophobic comonomer, which contributes surfactant-like properties, can provide better color acceptance with organic pigments (95–98).

For automotive OEM and car-refinish base coats, water-borne systems have become state of the art, especially in Europe. Due to the high demands on color strength, color accuracy, and color reproducibility in this branch the use of specialized dispersants is almost inevitable. The same is true for modern high-gloss decorative paints, which are progressively replacing traditional solvent-borne alkyd paints. In both cases, an excellent state of dispersion of the pigments is required, which is hardly achievable with traditional poly(carboxylic acid) (co)polymers.

5.11. Mineral Processing. Dispersants are used as mineral processing aids for grinding and improving slurry stability. Key mineral processes using dispersants include calcium carbonate and kaolin manufacture, and gold beneficiation. As a grinding aid, the dispersant reduces the amount of mechanical energy required to break down the ore to smaller particle size. For grinding, polyphosphates are frequently used because of their low cost. If the slurry is spray-dried to a powder, then little or no additional dispersant is required. If the mineral is kept in slurry form, then an auxiliary polymeric dispersant such as sodium polyacrylate is added to improve storage stability.

5.12. Caulks, Sealants, and Roof Coatings. These have similar technology to paints, except that they are formulated at higher solids to produce a thicker coating. As with paints, two types of dispersant are used; a primary dispersant such as KTPP (potassium tripolyphosphate) to disperse pigment agglomerates, and a secondary dispersant, such as sodium polymethacrylate, to provide storage stability of the formulation. The polyphosphate is a good dispersant for pigment, but hydrolyzes during storage to orthophosphate, which is not effective. Caulks, sealants, and roof coatings differ from paints in that they must minimize water leakage (permeance), but still allow water-vapor transport. Although water permeability of these films lessens with time due to leaching of water-sensitive materials such as dispersants, a variety of less sensitive dispersants have been developed to overcome this problem. Less water-sensitive dispersants include zinc sodium hexametaphosphate (primary dispersant), and hydrophobic polymeric dispersants (secondary dispersant) (99).

5.13. Agricultural Uses. Dispersants are used to formulate pesticides into aqueous dispersions (flowables), wettable powders, water-dispersible granules, and dry flowables. Aqueous pesticide dispersions or flowables are liquid suspensions of 20–50% active ingredient (AI), and usually contain wetting agent, thickeners such as polysaccharide gums, and dispersants. When the formulation is mixed in water, the AI particles can settle in spray tanks unless a dispersant is used to prevent settling and agglomeration of the pesticide before application. Powders, granules, and dry flowables contain AI, a carrier or diluent (eg, clay or silica), wetting agent, and dispersing agent. These formulations are diluted with water before spraying on crops. The dispersant keeps the AI uniformly suspended during application to provide uniform coverage and prevent nozzle clogging. Dispersants used include lignosulfonates, naphthalenesulfonate condensates, and sodium polymethacrylate (100). Another agricultural use of dispersants is in the production of animal feed, where lignosulfonate acts as a binder to enhance pelletizing.

5.14. Detergents and Cleaners. Dispersants function as builder assists (101,102) in cleaning formulations to increase particulate soil removal, prevent redeposition of soils to maintain whiteness or eliminate residues (spots) on hard surfaces, prevent precipitation of inorganic salts (carbonates, phosphates, and silicates), increase water-wettability of soiled surfaces, and promote physical stability of slurried formulations. They improve spray drying of powders by improving slurry (crutcher) homogeneity, increasing solids of crutcher mix (time and energy savings), reducing dusty fines, and increasing bead strength. Dispersants increase the rate of solution for powdered detergents and buffer the water to maintain optimum cleaning pH (see DETERGENCY).

A typical cleaning or detergent formulation contains surfactants (eg, linear alkyl sulfonic acid), builders (eg, sodium metasilicate, soda ash, polyphosphates), and dispersants [eg, polyphosphates, poly(acrylic acid)]. In fabrics, soil redeposition during cleaning leads to graying, and on glasses it leads to spotting and filming. Dispersants increase the Coulombic repulsive barrier around particles to enhance their removal from surfaces and inhibit their readherence (103,104). Historically, polyphosphates have been used as dispersants in detergents and cleaners. However, detergent manufacturers have been eliminating polyphosphate from some formulations due to its impact on eutrophication of lakes and streams. Revised cleaning formulations now contain a combination of inorganic builder and synthetic polymeric dispersant to replace polyphosphates (101,103,105). Non-phosphate detergents and cleaners that use soda ash as a builder can form calcium carbonate with the hardness in the water. The addition of polymeric dispersants to the formulation inhibits calcium carbonate precipitation on the fabric or surface.

6. Environmental Considerations

6.1. Biodegradability of Dispersants. Because many dispersants are water soluble, their environmental fate is less obvious to the general public than, eg, packaging plastic. Most reviews on biodegradable polymers suggest that, with the exception of poly(vinyl alcohol) and poly(ethylene glycol)s, most synthetic organic dispersants are recalcitrant in the environment (106). More recently developed dispersants displaying biodegradability are polymers containing ester linkages (107) and ether linkages (108). There is currently a great deal of research activity to develop dispersants that are both effective and biodegradable.

6.2. Future of Dispersants. The dispersant market has been changing continuously since the early 1970s. The primary driving forces in this market are environmental. Alkylphenol ethoxylates (APEs), which are widely used as dispersants and surfactants, are currently under pressure, especially in Europe, as their degradation products show estrogen-mimicking properties (109). There is a trend to eliminate chromate in cooling water (requiring high pH, dispersant-dependent formulations) and to remove ferrochrome lignosulfonate from drilling muds. In order to minimize air pollution due to the emission of organic solvents from paints, inks and coatings, more and more water-borne and high-solids paints replace traditional low-solids solvent-borne ones. This is only possible if the pigments used are well dispersed, which requires the use of specialized pigment dispersants.

If we continue the current trend, there will be an even greater need to provide highly effective dispersants with minimum environmental impact. Future development efforts will focus on improved performance at low dosage to further reduce the environmental load, accountability (ability to detect dispersants at ppm levels and minimize dose level), and, ultimately, biodegradability. Improved performance will mean ever more specialized dispersants to fulfill specialized technical requirements. The trend to eliminate organic solvents from paints, coatings, and agricultural formulations will continue.

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