

Rapid #: -25244127

CROSS REF ID: **29598098940002920**

LENDER: **EYW (Wayne State University) :: Main Library**

BORROWER: **CPS (California Polytechnic State Univ, San Luis Obispo) :: Main Library**

TYPE: Book Chapter

BOOK TITLE: Chemistry Materials and Properties of Surface Coatings: Traditional and Evolving Technologies

USER BOOK TITLE: Chemistry Materials and Properties of Surface Coatings: Traditional and Evolving Technologies

CHAPTER TITLE: 11 - Acrylic and Vinyl Resins

BOOK AUTHOR: Gündüz, Güngör

EDITION:

VOLUME:

PUBLISHER: DEStech Publications

YEAR: 2015

PAGES: 267 - 301

ISBN: 9781523147977

LCCN:

OCLC #:

Processed by RapidX: 9/17/2025 10:20:52 AM

This material may be protected by copyright law (Title 17 U.S. Code)

Acrylic and Vinyl Resins

ACRYLIC and vinyl resins have a very large market place in surface coating, and they can be used in the manufacturing of both solvent-based and solvent-free paints. Most of the architectural paints consumed worldwide are water-based acrylics. Acrylic resins show outstanding UV stability, good mechanical properties, particularly toughness, and excellent optical clarity.

Vinyl resins are obtained from the polymerization of monomers carrying a vinyl group ($\text{CH}_2=\text{CRX}$) where R and X can be anything. Acrylic monomers have either an ester ($\text{CH}_2=\text{CR-COOR}'$) or an acid group ($\text{CH}_2=\text{CR-COOH}$) instead of X. The number of acrylic monomers used for surface coating is much larger than vinyl monomers, and they are much more available and suitable for making surface coating resins than vinyl monomers. This is because ester groups have better adhesion properties than most other pendant groups. The ester groups have polarity which helps to establish sufficiently strong adhesion with the molecules of the coated surface.

Acrylic and vinyl monomers polymerized through additional polymerization mechanisms and the physical and mechanical properties of the resin produced depend on the chemical structure of a monomer, polymer chain length, and the size of side groups.

The acrylic resins and varnishes are highly transparent, and have high resistance against atmospheric conditions. They are resistant to water, chemicals, and alkalis, and they may be exceptionally flexible. They do not yellow at relatively high temperatures, and they have high gloss and good mechanical properties.

The types of monomers used, the chemical reactions involved, and

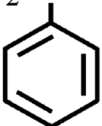
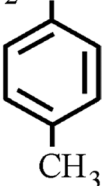
the production of latexes are discussed in this chapter, and the surfactants, thickeners, and other additives used are also considered. Brief information is given on hybrids and core-shell acrylics. Thickeners play a predominant role in the rheology of acrylic paints, and the technological developments in this field are still very active as well as the developments of new resins and hybrid acrylics. The high UV resistance of acrylic resins makes them indispensable in the production of UV resistant copolymers or hybrid coating materials.

11.1. MONOMERS

11.1.1. Types of Monomers

The properties of different acrylic and vinyl monomers are given in Table 11.1. Most of these monomers are liquid at room temperature, and they should be handled with care because they are toxic and flammable.

TABLE 11.1. Properties of Monomers.

Monomers*	MW	Formula	m.p. (°C)	b.p. (°C)	ρ
Vinyls					
Styrene	104	$\text{CH}_2=\text{CH}$ 	-30	146	0.91
p-methyl styrene	118	$\text{CH}_2=\text{CH}$ 	-24	167	0.926
Vinyl chloride	62.5	$\text{CH}_2=\text{CHCl}$	-153.8	-13.4	1.213
Vinylidene chloride	97	$\text{CH}_2=\text{CCl}_2$	-122	31.7	0.932

(continued)

TABLE 11.1 (continued). Properties of Monomers.

Monomers*	MW	Formula	m.p. (°C)	b.p. (°C)	ρ
Vinyls (continued)					
Vinyl acetate	86	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	-93	72.6	0.932
Acrylonitrile	53	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{CN} \end{array}$	-84	77	0.8
Metacrylonitrile	67	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{CN} \end{array}$	-35.8	91	0.85
Acrylamide	71	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{NH}_2 \end{array}$	84.5		1.122
Methacryl-amide	85	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{NH}_2 \end{array}$	108	215	1.11
Acrylates					
Acrylic acid	72	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array}$	14	141	1.06
Methacrylic acid	86	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array}$	15	161	1.02
Methyl acrylate	86	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_3 \end{array}$	-74	80	0.95
Ethyl acrylate	100	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$	-71	99	0.917
Butyl acrylate	128	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{C}_4\text{H}_9 \end{array}$	-64	146	0.984

(continued)

TABLE 11.1 (continued). Properties of Monomers.

Monomers*	MW	Formula	m.p. (°C)	b.p. (°C)	ρ
Acrylates (continued)					
Methyl methacrylate	100	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_3 \end{array}$	-48	101	0.939
Ethyl methacrylate	114	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$	-75	118	0.91
Butyl methacrylate	142	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{C}_4\text{H}_9 \end{array}$	-50	163	0.889
Isobutyl methacrylate	142	$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 \end{array}$	-61	155	0.886
2-hydroxyethyl acrylate	116	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-(\text{CH}_2)_2-\text{OH} \end{array}$	-60.2	192	1.107
2-hydroxypropyl acrylate	130	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \end{array}$	-92		1.044
Hydroxypropyl acrylate	130	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{O}-(\text{CH}_2)_3-\text{OH} \end{array}$	-30		1.06
2-hydroxyethyl methacrylate (HEMA)	130	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-(\text{CH}_2)_2-\text{OH} \end{array}$	-12	189	1.07
2-hydroxypropyl methacrylate (HPMA)	144	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \end{array}$	-58		1.066
Glycidyl acrylate	128	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \end{array}$			1.1

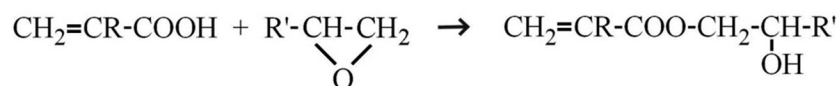
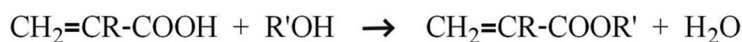
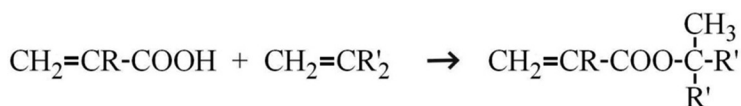
(continued)

TABLE 11.1 (continued). Properties of Monomers.

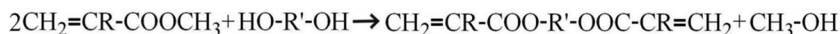
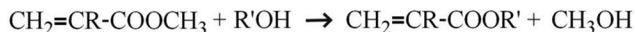
Monomers*	MW	Formula	m.p. (°C)	b.p. (°C)	p
Acrylates (continued)					
Glycidyl methacrylate	142	$ \begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\text{CH}-\text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \end{array} $		189	1.07
Ethylene glycol dimethacrylate	198	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_2 \\ \quad \quad \quad \quad \quad \\ \quad \quad \text{O} \quad \quad \quad \text{CH}_3 \\ \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \text{O} \\ \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \text{CH}_2-\text{O}-\text{C}-\text{C}=\text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \text{O} \end{array} $	-40	260	1.056
Diacetone acrylamide	169	$ \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{NH} \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \quad \\ \quad \quad \text{O} \end{array} $	55		

*MW: Molecular weight, m.p.: melting point, b.p.: boiling point, p: density

It is possible to synthesize other acrylates not given in Table 11.1 using different methods [1]. Acrylic acid can be reacted with other vinyls, alcohols, and epoxies to make new monomers:



The transesterification reaction of methacrylic esters with alcohols also gives new monomers:



11.1.2. Safety

Vinyl and acrylate monomers are generally toxic chemicals. Acrylamide and acrylonitrile can cause cancer, so the working environment must be well ventilated and monitored. The necessary precautions must be taken in the storage and handling, and close system handling must be done in plants. Anyway, their polymers are not mutagenic or cancerous.

11.2. GLASS TRANSITION TEMPERATURE

The selection of a polymer for the appropriate surface coating job depends on the physical properties of the polymer—actually, on the type of monomer. The price of the monomer is another factor that needs to be considered.

Acrylic homopolymers are rarely used in surface coating. The resin should meet the physical and mechanical requirements needed, and this can be achieved by mixing monomers at appropriate proportions to synthesize copolymers suitable for a surface coating job. For instance, a monomer which results in a very rigid polymer, and another one which gives a very soft polymer, can be mixed to synthesize a copolymer at appropriate hardness and appropriate glass transition temperature (T_g).

It was discussed in Chapter 2 that glass transition is a kind of second order phase transition, and the inner structure of a polymer abruptly changes due to change in the dynamical behavior of chains. The T_g of some polymers was given in Table 2.5; the T_g of acrylic polymers used in surface coating can also be found in that table.

The cross-linking effect on the hardness of polymers becomes important above T_g where disentanglements soften the thermoplastic polymers to large extents. The T_g values of copolymers can be experimentally determined, and it depends on the T_g values of homopolymers. Therefore, the monomers should be mixed at appropriate ratios to obtain a copolymer with the required T_g . There is a relation which gives the T_g of a copolymer in terms of the T_g s of homopolymers. It is given by:

$$\frac{1}{T_{gc}} = \frac{A_1}{T_{g1}} + \frac{A_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} denote the glass transition temperatures of the first and second homopolymers, respectively, and T_{gc} denotes that of copolymer. A_1 and A_2 represent the weight fractions of the monomers in the comonomer mixture, such that $A_1 + A_2 = 1$; and sometimes mole fractions are used instead of weight fractions.

11.3. PHYSICAL AND MECHANICAL PROPERTIES

Vinyl polymers are very resistant against heat, light, and chemicals. They are also resistant to hydrolysis although they have ester bonds in their structures. There is no tertiary hydrogen in methacrylates, and it makes them more resistant to UV radiation, hydrolysis, acids, bases, oxidizers, and corrosives over normal acrylates.

Some acrylates can decompose into their monomers at high yields when heated to high temperatures. This is possible if there is no hydrogen at α -carbon atom, such as in polytetrafluoroethylene, poly(methyl methacrylate), and poly(α -methyl styrene). The yield depends on the decomposition temperature, but it is possible to get yields as high as 95%. Poly(methyl methacrylate) is consumed in large quantities in the industry and it is also recycled to produce its monomer by thermal cracking. However, the regained monomer contains small fractions of organic compounds which act as a solvent (or plasticizer) upon polymerization.

The mechanical strength of acrylates is dependent not only on the molecular weight but also on the size of the side group, especially the size of the 'R' in the ester group of acrylate ($\text{CH}_2=\text{CR}-\text{COOR}'$). The T_g s of methacrylates are greater than those of acrylates until the carbon number in R' reaches 8–10. The methyl group in methacrylates enhances chain locking and strengthens entanglements and thus the cohesion. The side chains get longer as the carbon number in R' increases, and this keeps the backbones away from each other and decreases chain entanglements. The cohesion gets poorer and the polymer thus becomes softer; thus T_g decreases. However, on further increase of the length of side chains, entanglements occur between side chains, and the T_g starts to increase again. This occurs when the carbon number (i.e., $-\text{CH}_2-$ unit) in R' exceeds 8 in acrylates, and 12 in methacrylates. However, it does

not matter much for the polyacrylates commonly used in coating technology as R' is usually not big enough. The increase of interaction between side chains stabilizes chain motions in general, and segmental motion decreases; therefore T_g increases. So, depending on the length of side chains, T_g may decrease or increase, and this point needs to be taken into consideration when designing a copolymer at the molecular level.

Table 11.2 gives general information about the properties of acrylate homopolymers used in surface coating. The hardness of the polymer decreases as expected as the length of the side chain increases.

Paints used for exterior applications are exposed to severe atmospheric conditions and climate changes. Therefore, the resins used in the manufacturing of paints must not lose their flexibility for some years. To increase the flexibility by using plastifying agents is not preferred in surface coating because these substances have small molecular weights and drift up to the surface and leave off in time; however, they are used in some rare occasions. The copolymers can be designed at a molecular level to inherit plasticity. If one of the monomers used has a very low T_g , it acts as a kind of plastifier because its segments will have high mobility creating local softness. In an acrylic copolymer, the second monomer can be selected to have a longer side branch in the ester group of the monomer to produce softer binders. Acrylic monomers can usually mix at any proportion.

The fraction of monomers used also affects the adhesion strength of the copolymer. Adhesion depends on the flexibility of the chain, and also on whether the chains are linear or cross linked.

The resistance of acrylates against external effects increases with the

TABLE 11.2. Properties of Some Polyacrylates.

Property	MMA*	MA*	BMA*	EA*	BA*	2 EHA*
Hardness	High	Fair	Low	Soft	Quite soft	Very soft
Durability	Poor	Poor	Excellent	Fair	Very good	Excellent
T_g , °C	105	6	22	-24	-54	-70
UV resistance	Excellent	Poor	Excellent	Fair	Very good	Excellent
Gloss retention	Very good	Poor	Excellent	Fair	Very good	Fair
Humidity resistance	Poor	Poor	Excellent	Poor	Good	Good
Solvent resistance	Excellent	Very good	Good	Good	Fair	Poor

*MMA : methyl methacrylate polymer; MA : methyl acrylate polymer; BMA : butyl methacrylate polymer; EA : ethyl acrylate polymer; BA : butyl acrylate polymer; 2 EHA : 2-ethyl hexyl acrylate polymer.

total number of methylene ($-\text{CH}_2-$) and methyl groups on the chain. Methacrylates are more resistant than acrylates, as mentioned earlier, because they don't have tertiary hydrogen.

In Table 11.2, all properties except resistance to humidity and inter-layer adhesion smoothly increase or decrease as one goes from left to right. This can be explained with the methyl group and the increase of the length of R' in ester moiety. The chain backbones get away from each other as R' gets longer, and the cohesion gets poorer, yielding a soft material. The increase of the length of R' increases the solubility of polymer in solvents also because the solvent molecules can easily attack on linear side chains (i.e., "like dissolves like" principle) and solubility is facilitated.

Table 11.2 can be utilized to select proper monomers to synthesize copolymers of a desired property. In addition, vinyl monomers also can be mixed with acrylic monomers to further modify the copolymer. For instance, styrene can be added to improve hardness, gloss, and resistance against water and detergents. Acrylonitrile and acrylamide can be added to improve resistance against dust, dirt and solvents. Acrylamide additionally increases the hardness of the copolymer.

The availability of a rich variety of vinyl and acrylic monomers makes it possible to synthesize resins with tuned properties for very general purposes and highly special-purpose resins.

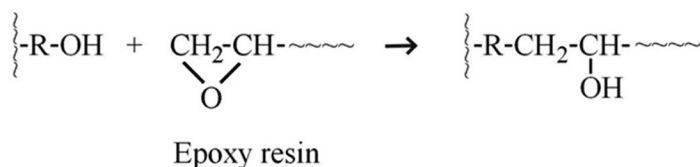
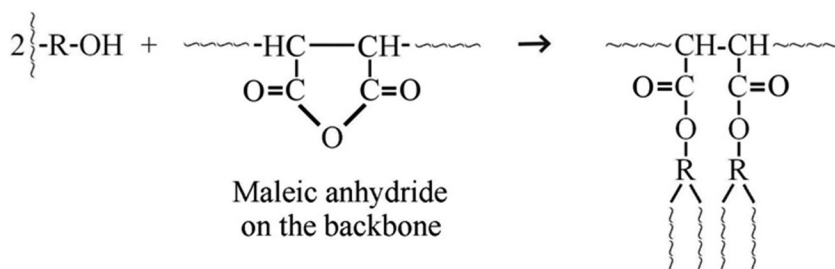
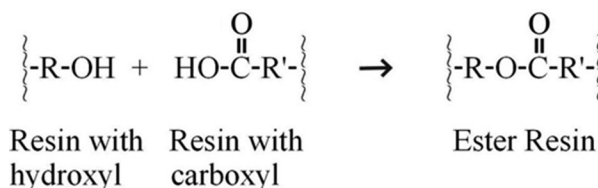
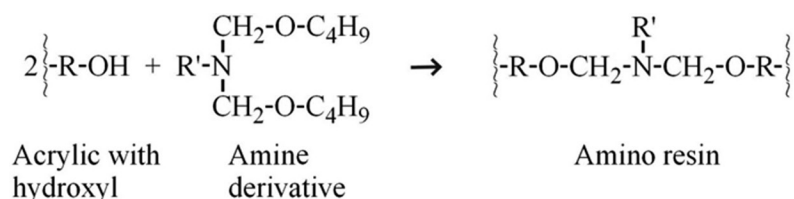
Acrylic polymers with modified surface properties can be synthesized by modifying the pendant groups on the backbone. For instance, a fluorine modified polymer can be manufactured by first synthesizing a copolymer using methyl methacrylate, butyl acrylate, and a functional monomer, namely 2-hydroxy ethyl methacrylate, and then esterifying the hydroxyl group with tetrafluoro propanoic acid at varying ratios between 4% and 10% [2]. Fluorination improves corrosion resistance of coating films. The perfluorobutylethylene introduced into the composition of paint decreases surface energy and gives stain release properties [3].

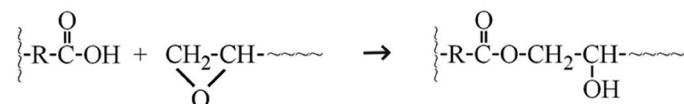
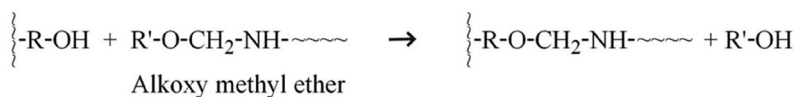
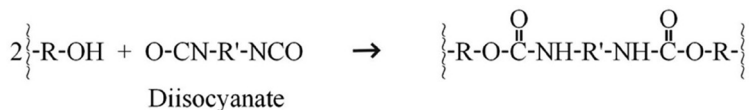
11.4. THERMOSET ACRYLIC POLYMERS

Thermoset vinyl or acrylic polymers are produced by using monomers having additional reactive groups. The monomer with a reactive group (e.g., comonomer) is added in small proportions to the main monomer. The polymerization is first carried through double bonds, and the reactive groups are thus introduced to the backbone. The type

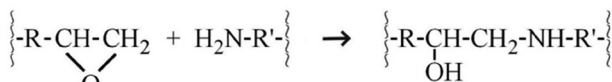
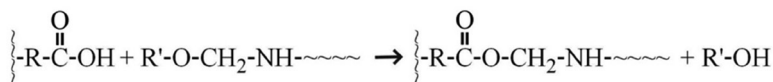
of monomer, chain length, glass transition temperature, solubility, miscibility, and frequency of occurrence of reactive monomer on the chain, etc., all affect the properties of the network formed. The surface coating materials manufactured by using network polymers naturally have higher hardness, toughness, and thermal and chemical resistance than thermoplastic polymers.

The functional group of the comonomer may be hydroxyl, carboxyl, amine, amide, carbamide, methylol, urethane, or epoxide depending on the expected properties. These groups chemically react with the groups of another polymer and form a network. Some examples are given below; the byproducts are not shown:



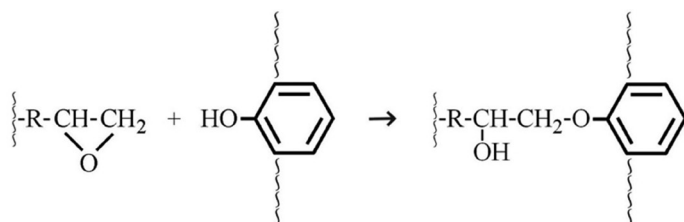
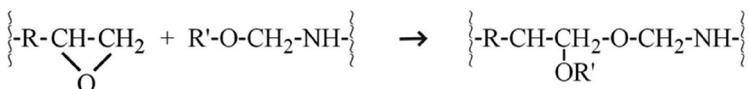


Acrylic with
carboxyl



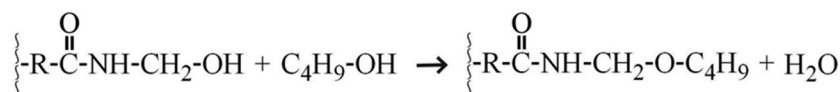
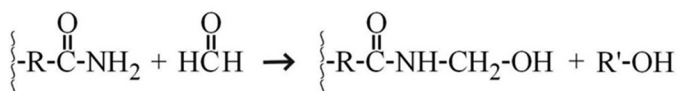
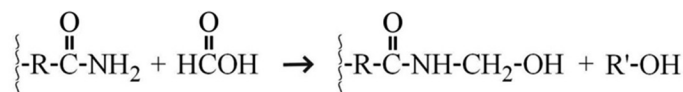
Acrylic with
Epoxy

Amine
resin

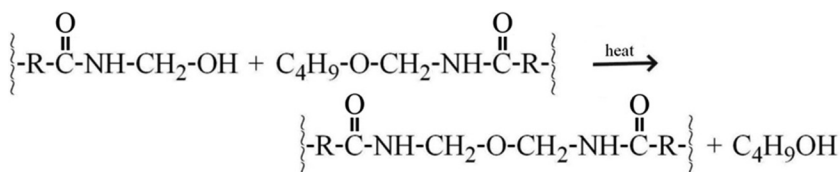


Phenol
resin

The resins with acrylamide can react with formaldehyde and form methylol groups. The product then can be reacted with butanol to form ether bonds:



These resins can undergo condensation reactions:



The product can undergo self condensation reaction, and form a network.

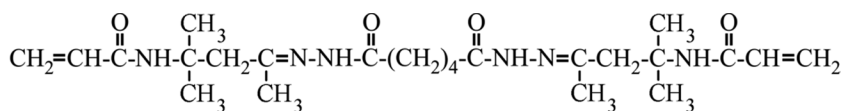
The resin with alkoxy methyl ether group can undergo self condensation and react with other resins having functional groups:



It is clear that there are too many possibilities for synthesizing acrylic network polymers by incorporating functional monomers into the backbone. The physical and chemical properties of the product can be tuned by mixing the functional monomers with the main monomer at appropriate proportions. The locations of functional groups control the internal structure and thus the strength of coating film [4]. The types of functional groups also naturally affect the properties of the network formed.

The types of catalysts to be used depend on the type of functional groups as discussed in former chapters.

The acrylic polymers can be self-cross-linked by using appropriate difunctional agents. The cross linking naturally increases the mechanical properties of the coating film. The use of polymerizable surfactants also contributes to the improvement of the properties. The cross linking is needed to improve the mechanical properties of waterborne acrylics; it can be acquired using small amounts of diacetone acrylamide monomer in the monomer mixture [5,6]. The -NH- on the pendant group provides cross linking upon curing. The reaction of two moles of diacetone acrylamide with one mole of adipic dihydrazide gives a diacrylate rich in -NH- groups:



It gives effective cross linking and thus a substantial increase in T_g when added to the monomer mixture [7].

11.5. THE POLYMERIZATION OF ACRYLIC MONOMERS

The resins used in the manufacturing of paints are synthesized usually by emulsion polymerization or solvent polymerization techniques described in Chapter 2. In either technique, the heat evolved needs to be taken into consideration to control the temperature in the reactor, and the reactor must be designed accordingly to provide heat removal.

The industrial manufacturing of resins is usually carried in batch reactors of 5–15 m³ of volume. Heating and cooling are performed by circulating silicon oil through the jacket around the reactor. Steam heating is preferred if the temperature to be held inside the reactor is low. The jacket is replaced with a flat coil in big reactors to achieve a better transfer of heat. The reactor is continuously agitated, and the volatile materials, especially the monomers, are condensed and sent back into the reactor by a condenser stationed at the top of the reactor.

The initiators are either mixed with a monomer or charged into the reactor. The monomer vapor in the reactor may be explosive on mixing with air, so all air in the reactor must be removed at the beginning by running nitrogen or argon through the reactor, and the polymerization reaction must be carried out under an inert atmosphere. The removal of oxygen also eliminates its retarding effect on radical polymerization.

The polymerization is usually over when 99% of the conversion

is achieved. The viscosity measurements can give an idea about the molecular weight and the state of polymerization. The duration of polymerization depends on the reactivities of monomers, and may vary between 5 and 30 hours.

The molecular weight of thermoplastic resins should not be increased above 120,000–130,000; otherwise, there will be intense entanglements and the paint surface will not be very smooth.

The molecular weight of prepolymers to be used in the manufacturing of thermoset paints must be in between 20,000 and 30,000. Low molecular weight resins need a lower amount of solvents.

11.5.1. The Manufacturing of Resins by Solvent Polymerization

Monomers including inhibitors must be purified if the inhibitor does not decompose at the polymerization temperature. Therefore, the removal or inactivation of inhibitors is essential to synthesize chains of sufficiently long length. In solvent polymerization, solvent molecules can act as chain transfer agents and small molecular weight chains are synthesized. However, the chains need not be too long for surface coating jobs, and especially in manufacturing inks. The molecular weight less than 150,000 is acceptable for many applications. For such applications it may even be possible not to remove inhibitors and also use excess initiators to accelerate the polymerization; small molecular weights are obtained in either case.

The monomer and solvent are mixed at more or less equal proportions, and appropriate solvent must be used; for instance, ethyl acetate is used to synthesize poly(vinyl acetate) from a vinyl acetate monomer. Methyl ethyl ketone and methyl butyl ketone or their mixtures with toluene can be used as a solvent for acrylates.

The reactivities of monomers differ from each other, and the order of the frequency of monomers at the backbone of a copolymer is determined by monomer reactivity. That is, the composition of copolymer chains in the early and late periods of polymerization may differ, and the properties of a synthesized copolymer may change accordingly. The monomeric composition of a chain can be controlled by adding one of the monomers in parts during the course of polymerization within few hours. The retarded additions regulate the monomer concentration in the medium, and thus the frequency of occurrence of monomer units at the copolymer chain.

As can be deduced from Table 11.2, hard resins can be synthesized

by preferring methyl methacrylate in the monomer mixture, and soft resins by preferring butyl acrylate. The resin with a hydroxyl functional group can be obtained by using 2-hydroxy acrylates. Its molar fraction can be as high as 20% in general purpose surface coating resins. A resin containing both hydroxyl and carboxylic groups can be prepared by using both 2-hydroxy acrylates and acrylic acid in the monomer mixture. The acrylic acid is added at low quantities, less than 5%. The polymerization temperature of such a mixture can go up to 130–140°C because acids lower the rate constant. Additional initiators may be added in time, especially towards the end of polymerization to achieve high conversion.

Resins with aromatic units exhibit relatively poor adherence on metal surfaces compared to aliphatic resins. So it is recommended that styrene should not be used in the synthesis of such resins; a mixture of methyl methacrylate, ethyl acrylate, acrylonitrile, and acrylic acid can be used in the manufacturing of resins for coating metal surfaces. Methyl methacrylate is around 75% and acrylic acid is less than 5% in the monomer mixture.

Thermoset resins can be prepared by introducing 4–5% acrylamide in the monomer mixture. Formaldehyde is added to change -NH_2 into $\text{-NH-CH}_2\text{-OH}$; thus hydroxyl groups are created on the backbone of resin. Butanol and toluene are used as solvent at equal proportions. Acrylamide and formaldehyde are first dissolved in butanol at around 50°C, and then toluene as a cosolvent and phosphoric acid (~0.2 %) as a catalyst are added. Then the temperature is raised to 85–90°C. Then the monomer mixture containing styrene, ethyl acrylate, butyl acrylate, and acrylic (or methacrylic) acid is added together with an initiator like benzoyl peroxide, and the temperature is raised to 110°C. A conversion of 99% must be achieved; if not, some more initiator may be added in the late periods of polymerization.

Thermoset acrylic resins and aliphatic polyisocyanates can be mixed to manufacture an automotive top coat varnish. The polyisocyanate makes about 10–15% of the mixture. These resins can be mixed with titania to manufacture furniture white paints. Some other resins discussed in previous chapters may also be blended with acrylic resins to manufacture thermoset varnishes and paints.

11.5.2. The Manufacturing of Latex Paints

Most of the architectural paints used at homes, offices, and buildings

are emulsion paints manufactured from poly(vinyl acetate), polyacrylates, and copolymers thereof. The introduction of such paints has been a revolutionary development in paint technology. The traditional use of lime or any other natural materials and binders used to cause some adhesion problems, and they didn't last for sufficiently long times. The use of oil paints was a difficult operation, and the surface had to be flattened first by applying putty which is made from boiled linseed oil and clays and lead oxides. That was a time consuming and expensive operation, but cracks could occur otherwise. In addition, oil based paints and alkyd paints can easily blister if there is severe humidity in the wall. There is no need to have flattening and surface finish on the wall when coated with emulsion paints. They can be directly applied on any material whether it is plaster, grout, lime, etc. They transfer humidity from one side to the other; that is, the paint film is permeable to water vapor, and so they are very durable on the wall.

11.5.3. Production of Poly(vinyl acetate)

A conventional batch reactor equipped with a back condenser is used in the production of poly(vinyl acetate). Vinyl acetate and water are added near equal proportions.

Poly(vinyl alcohol) (PVA) which is 88% hydrolyzed is used around 1–2% to emulsify the monomer. It is first dissolved in water, and the temperature may be increased up to 90°C. Although PVA looks highly hydrophilic, it is difficult to dissolve in water because rich hydroxyl bonds of PVA make hydrogen bonds within the structure, and water molecules cannot easily break into these already established bonds. PVA solution, sodium acetate, catalyst, and about 10% of vinyl acetate is charged into the reactor. Then the temperature is raised to 70–75°C. Excessive foaming may take place at the beginning because of PVA which seriously increases surface tension. The rest of the vinyl acetate is slowly charged into the reactor in 1–2 hours. The temperature is increased to about 90–95°C to reduce surface tension towards the end of reaction to acquire agglomeration of very fine particles. A milky product with a pH of about 4–5, and with a viscosity around 20 Pa·s is obtained; the particles have an average size of 0.7–0.8 µm. The particles produced are stabilized by PVA. The emulsions thus manufactured are called *latex*. The duration of time needed for emulsion polymerization is lower than the time needed for solution polymerization.

The generally used terminologies may lead to confusion as they all

signify similar structures but at different sizes. The *dispersion* denotes very finely fragmented solid particles in water with very high solid-liquid interfacial area. *Emulsion* denotes the dispersion of one immiscible liquid phase in another phase, notably, water which is a continuous phase. *Latex* is the colloidal dispersion of a solid polymer in water resulting from the polymerization of an immiscible monomer in water. *Suspension* is the noncolloidal dispersion of a solid in liquid phase, and the solid particles are relatively big so that the solid-liquid interfacial area is quite small [8].

Instead of PVA, it is possible to use some other emulsifying agents like hydroxy ethyl cellulose and nonyl phenol. The conversion achieved using ammonium persulfate as an initiator is around 95%. It can be increased to 99% by using hydrogen peroxide (~10% solution) and sodium thiosulfate (~0.1%) as an initiator. The product thus obtained has a pH value close to 5, a viscosity of 1.5 Pa·s, and an average particle size of about 0.5 μm . The reaction is completed in about 3 hours. The small angle X-ray scattering (SAXS) shows that the latex particle has a kind of shell with 2 nm thickness at the very outer surface [9].

Vinyl acetate can be copolymerized with acrylic monomers to modify the properties of poly(vinyl acetate) [10]. Another monomer used in copolymerization is maleic anhydride which may be esterified first with alcohols like butanol, benzyl alcohol, etc., and then copolymerized with vinyl acetate. Emulsification can be accomplished by using a mixture of lauryl alcohol and poly(vinyl pyrrolidone). The latter may also be used alone, but in that case the viscosity becomes low. The reaction may take 4 or 5 hours.

Poly(vinyl acetate) resins need plastifying agents although plastifiers are very rarely used in surface coating. Glycerol or ethylene glycol can be used for this purpose.

11.5.4. The Manufacturing of Polyacrylates

Polyacrylate latexes are also manufactured by emulsification in water using emulsifying agents and catalysts [11,12]. The water to be used must be deionized; otherwise the ions in water can saponify the carboxyl groups of acrylic acids if there is any in the monomer mixture. Sodium lauryl sulphate (~1%) can be used as emulsifier, and as catalyst, ammonium persulphate and sodium bisulfide are used at equal proportions (~0.4%). Water makes up a large portion of the emulsion, about two-thirds of the total.

The monomer composition in the reactor changes in time due to the difference in the reactivities of monomers. So the monomer mixture must be charged into the reactor slowly as to not to disturb the chain composition severely in time beyond expectations. It may take 2 or 3 hours depending on the reactivities of monomers and thus on rate constants of polymerization. The polymerization is carried out at 60°C and the temperature is raised to 90°C in the last stage of polymerization to accomplish the conversion of all remaining monomers.

The polyacrylic latex containing styrene is consumed in large quantities in the industry even though there is a decreasing interest in its use. It is synthesized using styrene and butyl acrylates at equal proportions and acrylic acid (~2–3%). It is emulsified in water in a tank using a surfactant (~2%) and a colloidal agent (~2%). The amount of water used as a dispersing medium makes about two-thirds of the total content. The reactor is first charged with water at about 25% of the total material in the tank, and catalyst and colloidal agents like ammonium persulfate and ammonium hydroxide are added. Polymerization can be started with a small fraction of a monomer, and the rest is added in about 2 hours. Some additives, like antifoaming and biocides, may also be introduced into the reactor. Then the material in the tank is added slowly into the reactor within about 2 hours. The reaction is carried out at 80–90°C. After the reaction is over, redox agents like L-ascorbic acid and t-butylhydroperoxide can be added to reduce the residual monomer. The latex produced is filtered out for final dispatch.

Water dispersed acrylic resins may also be produced by the same procedure. In this case, aromatic styrene must be substituted with aliphatic acrylate monomers. To have sufficient hardness for the resin, ethyl acrylate may be used. In addition, acrylic acid must be used at large quantities (~20%) to have dispersion in water. The fractions of butyl acrylates and other acrylates are adjusted in accordance with the desired physical and mechanical properties of the resin.

The type of protective colloid used affects the properties of latex and the coating film. The N-methylol acrylamide oligomer compared to poly(vinyl alcohol) used in the synthesis of copoly(vinyl acetate/butyl acrylate) gives lower viscosity, lower polydispersity, finer particle size, and higher T_g [13].

The acrylic acid used in the comonomer mixture does not ionize at pH = 3–7, but ionizes at pH > 7. The increasing pH dramatically affects the particle morphology [14].

11.6. ADDITIVES OF LATEX PAINT

So far, two different mechanisms of the hardening of surface coating materials have been discussed. The resins which contain unsaturated bonds, like oil based resins and alkyd resins, harden by picking up oxygen from air and forming cross links. The second mechanism which is much more common than air drying involves the reaction between reactive groups forming a network.

It is also possible to incorporate reactive groups into vinyl and acrylic resins which then can form network structure. However, most acrylic based resins are thermoplastic polymers, and they dry physically. The latex paints used at homes dry out by the evaporation of water, and no chemical reaction takes place.

11.6.1. Surfactants in Latex

In emulsion systems, the polymer particles have a diameter around half a micron suspended in water. Their stability is achieved by the surfactants on the surface of particles and by colloidal agents. Surfactants can be ionic or polar, and can easily interact with water which is the dispersing medium. The ionic or polar part of the surfactant molecule is headed outward to the water phase. Therefore, the particles repel each other as they carry the same charges. Upon application of latex paint on a wall, water is removed through absorption by the wall or through evaporation, and then oppositely charged ions of ionic surfactants recombine. The miscibility of ionic surfactants in a polymer may be poor after drying. This may cause heterogeneity at a micro level, and possibly turbidity in color. Nonionic surfactants like polypyrrolidone are usually miscible with polymer, and they don't much affect the transparency of the polymer.

The addition of pigments into waterborne latex can change the viscosity of paint. Pigments to be used in latex paints are surface modified with surfactants and dispersants to minimize flocculation and settling. Pigments are stabilized in waterborne latex by steric or electrostatic effects caused by surfactants.

Latex paints also contain *thickeners* which lead to a very high increase in viscosity. In recent years a new group of thickeners called *associative thickeners* have been highly popular. They form interactions with pigment particles and with each other. Associative thickeners actually form a physical network and cause a dramatic increase of viscosity.

The surfactants of pigments and coloring agents can interact with thickeners and affect the network formed and thus the rheology of paint. The mutual interaction may not be significant at low levels of pigments but may be important as the amount of pigment increases to achieve better color tones. The problem can be solved by changing the type of surfactants and dispersants used [15].

Surfactants can also improve color development [16]. Eco-friendly, biodegradable surfactants mostly derived from renewable resources are finding increased acceptance by paint manufacturers [17].

Besides providing dispersion stability, surfactants also improve shelf life, freeze-thaw stability, and mechanical stability, and they can improve the adhesion of coating on the substrate as well. However, they may decrease the water resistance of coating, and polymeric surfactants can cause blistering on the coating film [18]. The freeze-thaw stability of latex coatings can be achieved by using copolymerizable reactive monomers [19].

It is also possible to use reactive surfactants in latex. They are covalently bound to the polymer phase rather than through Van der Waals interactions [20].

11.6.2. The Effect of Solvents

The polymer particles get close to each other upon removal of water, and they combine with each other forming a film. The surface tension of particles must be low enough so that they can overcome the activation energy of combination and thus form a uniform film through coalescence. The presence of small amounts of polar solvents expedites the film formation. For instance, ethylene glycol is a polar compound and is miscible with water and hydrophilic polymers. In the course of drying, water captured inside escapes from the coating film by diffusion which is a very slow process. Ethylene glycol molecules get close to the hydrophilic groups and cause local swelling. The captured water molecules then migrate more easily to the surface and leave the coating film.

The colloidal agents and other additives accumulate in micro voids between the coalesced particles. Filling of micro voids improves the mechanical property of coating film.

11.6.3. The Retardation of Drying

The amount of pigments used in latex paints is lower than the

amount used in solvent based paints. The pigments used must not dissolve in water. Some of them may have surface active agents which provide better dispersion in organic solvents. However, if these pigments are used in latex, the surface active agents may interact with surfactants and destabilize the emulsion. Due to removal of some surfactant molecules, particles combine with each other and undergo phase separation.

Additives that retard evaporation are usually introduced into latex paints. In wet paints, the period in which the irregularities can be repaired without brush marks is called *open time*, and the period in which a second coating can be applied over the first one without leaving marks is called *wet edge time*. These periods are important as the aesthetic appearance is of primary concern. Some additives can be used to control these periods [21]. The second coat application must be done before the first coat is dried. If polymer particles of the first coat completely coalesced, they may not effectively adhere to the molecules of second coat. Fast coalescence can be slowed down by retarding the evaporation of water. For this purpose, some chemicals like ethylene glycol, propylene glycol, and higher glycols may be used. These glycols affect colligative properties of water, and lower the vapor pressure. Hence, the evaporation rate of water is lowered. The pedestrian's practical and trivial solution is actually to mix latex paint to be used in the first coat with relatively large amounts of water.

Some filler materials, such as sodium montmorillonite clay in a latex system, slow down the rate of film formation. The presence of clay increases the activation energy needed [22].

The additives for freeze-thaw stability can also be needed by solvent free latex paints to prevent destabilization during transport, storage, and application as the resins used in these paints have lower film forming temperatures [23].

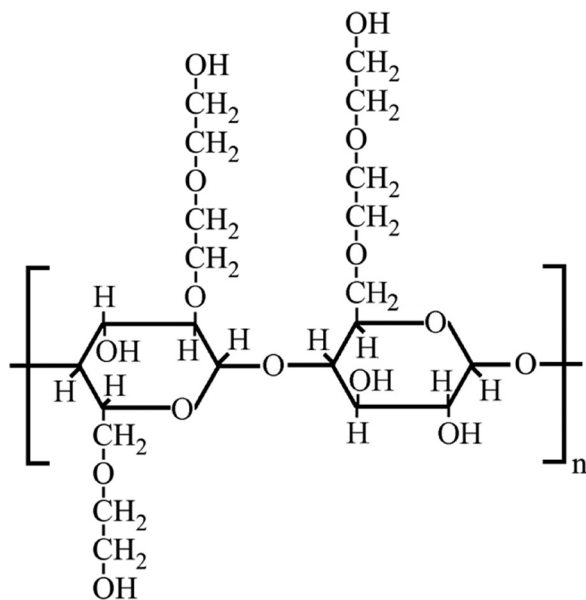
11.6.4. Thickeners

One of the most important additives used in latex paints is a viscosity increasing agent called a *thickener*, which actually minimizes the random motion of colloidal particles and prevents their coalescence. They are added to control the application viscosity and the sag and slump resistance. Only 3–4% of cellulose ether in water yields a quite thick transparent gel and minimizes the settling of pigments.

11.6.4.1. Water Phase Thickeners

Thickeners can be of both organic and inorganic origin, and clays are known to be the best inorganic thickeners. Clay particles yield a gel in water-forming hydrogen bonds with the hydroxyls on the surface of clay platelets.

The most common chemicals that increase the viscosity of water are cellulose ethers. The most widely used ones are: hydroxyethyl cellulose, methylhydroxyethyl cellulose, ethylhydroxy ethylcellulose, hydroxymethyl ethylcellulose, methylhydroxypropyl cellulose, and carboxymethyl cellulose. The formula of hydroxyethyl cellulose is:



Among these ethers, the hydroxyethyl cellulose is the most consumed thickener in the industry, and it has the highest water retention capacity. The molecular weight of cellulose ethers is much more important than the substituents on the cellulose backbone. Carboxymethyl cellulose contains sodium and it is used in cheaper ceiling paints.

11.6.4.2. Associative Thickeners

Associative thickeners thicken the paint through interaction with other paint components. They increase the viscosity through hydropho-

bic interactions. The incorporation of thickeners with alkyl or alkylaryl groups introduces hydrophobic units to the thickener molecule. The hydrophobic units are involved in two different types of hydrophobic interactions. The first is their interaction with the binder molecules, and another is their interaction with each other. Therefore, within the aqueous medium, the thickener molecules form a physical network between binder chains. It in turn delivers a very high increase in viscosity. The concentration of hydrophobic units usually does not exceed 2%. Since the thickener molecules are involved also in hydrophilic interactions whatever included in the paint whether it is binder, pigment, water, or surfactants all are somehow immobilized by hydrophobic and hydrophilic interactions. Compared to conventional thickeners, the associative thickeners deliver better flow, opacity, and gloss as they form better association with the latex particles, and lead to the more uniform distribution of the latex on substrate [24].

11.6.4.3. Polyurethane Thickeners

Polyurethane thickeners contain nonionic hydrophobic polymers in their structure and hydrophobic blocking components. Their molecular weight changes between 10,000 and 50,000; they are obtained from the reaction of diisocyanates with diols, and the blocking groups can be -NHR [25]. The polyurethane molecule contains both hydrophilic and hydrophobic units on the chain. Therefore, either unit can interact with the hydrophilic or hydrophobic parts of binder molecules or pigments. In addition, the hydrophilic parts interact with water and the hydrophobic parts form microdomains in water. In this respect, polyurethane thickeners can be considered to be associative thickeners.

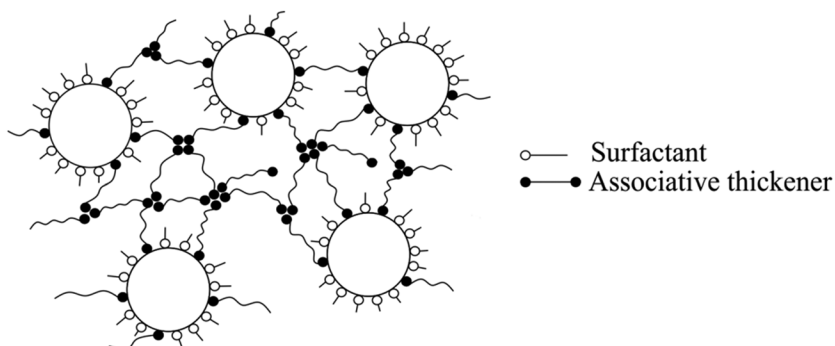


FIGURE 11.1. The action of associative thickeners.

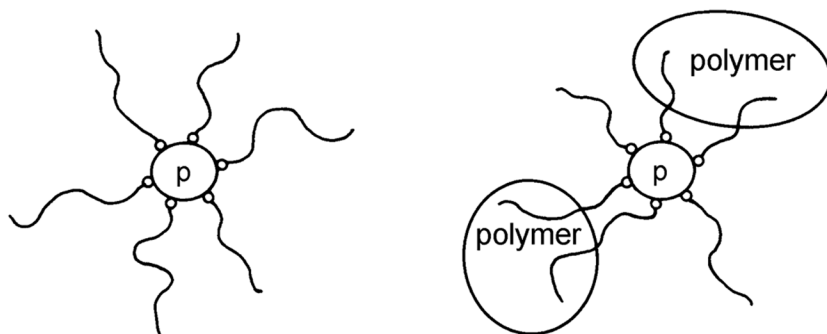


FIGURE 11.2. The surfactant-pigment-polymer interaction.

11.6.5. Wetting Agents

The surface active agents on pigments also help suspension in the dispersing medium. The charged (or highly polar head) of the oligomeric surfactant molecule attaches on a pigment particle as seen in the first sketch of Figure 11.2, where '*p*' denotes the pigment particle, and chains denote the oligomeric surfactant molecules.

The hydrophobic tail of the surfactant penetrates into the polymer particle according to the "like dissolves like" principle. Thus a bridge is established between the pigment and polymer as seen from the second sketch of Figure 11.2. Pigment particles are denser than polymer particles. As pigments are attached to polymer particles the density of the pigment-polymer cluster becomes lower than the density of the sole pigment. In other words, the *pigment-polymer* cluster needs smaller buoyancy force to float. The increase of viscosity of the aqueous medium by thickeners also increases buoyancy force, and pigments can suspend in the medium.

After the application of paint on a surface and subsequent drying, surfactant molecules pull the polymer chains towards the pigment particle. After the removal of water molecules, the surfactant chains undergo random bendings and fill the interspace. It spontaneously occurs because a bent chain has larger entropy than a relatively linear chain. In consequence, contraction takes place and pigment and polymer particles get closer to each other. Such surfactants are intentionally used for this purpose and they are called *wetting agents*. In cold weather, the polymer phase contracts and may separate from pigments. Surfactants or wetting agents resist contraction, retain the bridge formed, and prevent the separation of a polymer and pigment. As polymer phase contracts,

the distance between polymer and pigment particles increases, but the randomly oriented surfactant molecules or other molecules expand like a spring and keep attaching the polymer phase to pigment particles.

11.6.6. Antifoam Agents

Antifoam agents are added into paint to prevent the formation of foams, or eliminate them, eventually causing internal contraction. They are actually chemical molecules decreasing surface tension. The organic content of surface coating materials like polymers and oligomers all increase surface tension because these materials have chain structures and they form relatively stable configurations through side interactions or entanglements as seen in Figure 11.3. So foams, once formed, survive for a while.

Antifoam agents weaken the interactions between the big molecules and the relatively stable configuration is loosened. So the foam never forms or easily collapses. There is a variety of molecules which can function as the antifoam agent, but in the surface coating industry organophosphate compounds are frequently used.

11.6.7. Other Additives

In order to improve the properties of water based coatings close to that of solvent based paints, coalescing aids are added into water based paints. These additives may have branched structures also carrying hydroxyl groups which soften latex particles so that they fuse easily with each other [26]. Some other additives, like antifoam agents, and biocides, such as benzoic acid derivatives, are also added into latex paints. Vinyl acetate and vinyl chloride are susceptible to heat and light. The copolymers having these monomers in their structure may be mixed with calcium carbonate or other alkaline pigments or filling materials

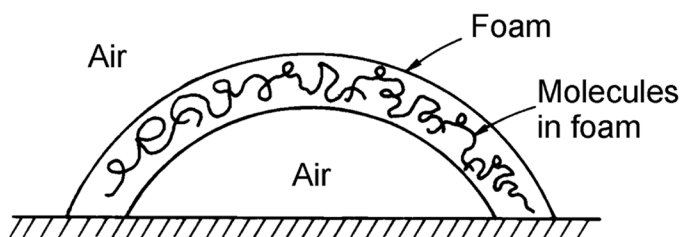


FIGURE 11.3. The structure of foam.

in the manufacturing step to reduce the adverse effects of heat and light. The copolymers with styrene units at the backbone are affected from UV light. The addition of UV absorbers is helpful to reduce such effects.

In old times, corrosion inhibitors like sodium benzoate were added to paint sold in metallic containers. However paints are now available in plastic containers and there is no need to add such additive. Corrosion inhibitors are added if the paint is manufactured for metal coating.

Water used in emulsification should not contain ions if acid monomers are used in the synthesis. Metallic ions make soaps with organic acids, and multivalent cations—especially calcium and magnesium present in hard water—react with neighboring carboxyl groups of different chains and establish a kind of cross linking. In turn, it increases the viscosity of the resin. So, deionized water must be used if there are acid monomers in the monomer mixture. In addition, strong reducing agents like sodium nitrite must be added into paint.

Poly(vinyl acetate) can undergo hydrolysis and the viscosity decreases in time. The addition of the propyl or butyl alcohol or thiocyanates lowers the rate of hydrolysis and the change of viscosity in time is minimized.

If polyvinyl acetate with a high hydroxyl content is used as the resin, it is vulnerable to the attack of water. Water resistance can be increased by adding small amounts of borax or glyoxal. These molecules establish cross-linkings and the resin achieves higher resistance.

A number of harmful or undesired volatile organic compounds (VOCs) like formaldehyde are emitted from the furniture which uses phenol or urea/melamine formaldehyde resins, and it lowers the quality of indoor air causing *sick building syndrome*. Some materials like chitosan can be introduced into acrylic emulsion to fight such problems. The amino group in the structure of chitosan reacts with formaldehyde and removes it [27].

11.7. ACRYLIC PAINTS

Acrylics are mainly used for general purpose surface coating jobs, but they can also be used as flexible clear coats for coil coating [28]. Acrylic paints are prepared in two steps. The first step involves grinding the pigments together with some additives. Pigments such as titania (~5–20%), water (~10–30%), clay based colloidal agents like sodium or potassium aluminum silicate (~5%), thickeners like hydroxyl cellulose (~10% of 1–3% gel), grind aids (~0.5%), and wetting agents

(~0.3%) are mixed and ground. It is then mixed with another batch containing acrylic emulsion (~10–50%), ethylene glycol (~1%), an antifoam agent (~0.3–0.8%), a wetting agent (~2%), biocides (~0–0.3%), and ammonium hydroxide (~0.3%). The percentages given here for two batches should total up to 100%. These percentages change depending on whether the paint will be used for internal or external use. These figures give a rough idea only.

The volume of pigment is about one-third of the total volume, and the total solid content (pigment plus organics) is about 50%. The pH of emulsion paints is kept around 8 or higher, and it is achieved by adding ammonium hydroxide.

The compositions of several waterborne acrylic formulations are given in Table 11.3. Pigment volume content may drastically change depending on the type of application.

TABLE 11.3. Formulations of Some Architectural Paints.
(Courtesy of BETEK BOYA ve KİMYA SAN. A.Ş., İstanbul.)

Material	#1	#2	#3	#4	#5
Water	15	21.05	10.88	20.21	28.03
Polyphosphate (dispersion agent)	0.1	0.1	0.1	0.1	0.05
Hydroxy ethyl cellulose (thickener)	0.1	0.2	0.2	0.25	0.3
Ammonia solution (25%, for pH adjustment)	0.2	0.05	0.02	0.04	0.02
Ammonium polyacrylate (40%, dispersion agent)	0.5	0.3	0.5	0.4	0.3
Antifoam agent (mineral oil based)	0.6	0.2	0.6	0.5	0.3
Titania (TiO ₂ white pigment)	20	10	20	11	6
Calcite (CaCO ₃ extender)	5	45	11	50	56
Calcined clay (filler)	–	–	1	–	4
Aluminum silicate (filler)			5		
Organic opacifier	15	5	7	4	56
Polyurethane emulsion (thickener)	0.2	0.3	0.4	0.2	0.1
Binder*	40	15	40	12	4
Antifreeze agent	–	1	–	–	–
Film former	3	1.5	3	1	0.6
Biocide	0.3	0.3	0.3	0.3	0.3
Total	100	100	100	100	100

*formulation #1: acrylate emulsion, 50% in water.

formulation #2, 3, and 4: styrene-acrylate copolymer, 50% in water.

formulation #5: vinyl-acrylic emulsion, 50% in water.

**PVC: pigment volume content.

#1: outdoor (35% PVC); #2: outdoor (60% PVC); #3: indoor (40% PVC); #4: indoor (65% PVC); #5: indoor (90% PVC).

The addition of nanosilica to acrylic latexes improves the mechanical properties and the hardness of the coating film [29]. The use of acrylic resins in road marking has gained significant importance within the last two decades. The pigment volume concentration, abrasion resistance, hardness, gloss, and drying time need to be optimized to prepare a good quality road marking [30].

Acrylate polymers usually have high permeability to moisture. The copolymer emulsion containing ketocarbonyl, amide, and carboxyl groups have a high capacity for absorbing humidity. The coating has a porous structure, and water can easily go in and out giving a kind of indoor humidity control [31]. For this reason, polyacrylates are one of the best paints for indoor use.

The latex paints containing acid functionality due to acidic monomers like acrylic acid and its degree of neutralization greatly affect the dispersibility of pigments and deliver better dispersion. The increase in the number of acidic groups also increases the scrub resistance [32].

Another important use of acrylic latexes is in the production of artist paints, and about half of the artist paints currently consumed worldwide are of acrylic origin [33].

11.8. WATERBORNE ACRYLICS

Waterborne acrylics paints differ from emulsion paints in the way that polymeric material disperses in water. In traditional emulsion paints the emulsification is carried out by using external emulsifiers, whereas in dispersion paints internal emulsifiers are used.

The logic behind these paints is to incorporate highly hydrophilic components into the backbone to make it dispersible in water. Polymers can be made waterborne by three different mechanisms. The first one is direct dissolution of small molecular weight polymers (20,000–50,000) in water, and the size of dispersed particles is smaller than 5 nm. The second method is to form colloids in water, and the polymer chains with molecular weights between 20,000–200,000 can be dispersed in water by forming colloids. Small molecular weight polymers dissolved in water are usually transparent while the medium molecular weight polymers forming colloids become opaque.

The third mechanism is to disperse polymer chains which may have a molecular weight up to one million in water. The size of dispersed particles may be larger than 200 nm. The viscosity of water dispersed paints is low as the viscosity is controlled by the dispersant—that is, the

water phase. In solvent based paints, viscosity heavily depends on the molecular weight of the binder polymer dissolved in solvent because chains are decoiled in solvent and they entangle and increase the viscosity if solvent is sufficiently reduced. In waterborne paints, chains are in a dispersed phase and the water phase does not significantly affect the chain configurations in the organic phase.

Waterborne paints form relatively more rigid films than solvent based paints because of already established chain entanglements before applying on a surface. In other words, there is already cohesion between chain molecules that in turn reduces the adhesion on a substrate. For the same reason, they may not establish strong bonds with pigment molecules. All these affect the physical properties, and the waterborne paints usually have less gloss than solvent based paints. The physical properties of colloid paints lie between solvent based and water dispersed paints. They are very commonly used in a large number of applications, and are well accepted by customers. Actually, there is a very strong tendency to prefer water based paints by consumers for environmental awareness, and paint producers have shifted to waterborne paints to avoid losing their market shares and due to regulatory pressures to reduce solvent emissions as well.

The dispersion of polymers in water can be achieved by introducing hydrophilic groups like carboxylic acid groups and amines to the polymer chains. These groups are stationed either as monomeric units at the backbone or as side groups. The carboxyl and amine groups are neutralized to obtain highly soluble organic salts to increase the extent of dispersibility.

In waterborne acrylics, the monomer composition needs to be prepared with care because the physical, mechanical, and the chemical properties of the coating film depends on the monomers used to a great extent. Methylacrylate and ethylacrylate are not often used in the mixture because methylacrylate can be easily hydrolyzed and ethylacrylate has a strong bad odor. The T_g of the polymer is usually tuned by mixing with butylacrylate, methyl methacrylate, and 2-ethylhexyl acrylate. Styrene was heavily used in the past but its use is limited because it has a low rate of polymerization and some monomers remain unreacted. The copolymers of styrene with acrylic acid, methacrylic acid, and itaconic acid, which has two carboxylic groups, can be used to make latex paints and also can be functionalized with epoxide group for increased thermal stability [34,35].

The use of some monomers with functional groups, such as the use

of methacrylic acid, serves to establish cross linkings when blended with other resins like urea or melamine resins.

Emulsifying agents must be used in small quantities to decrease the hydrophilicity of the polymer. It is known that polymers with narrow size distribution need less emulsifying agents; so chain transfer agents such as tertiary dodecylmercaptane must be added at around 1% to the monomer mixture. It also helps to achieve fusion of particles easily during drying.

The shelf life of waterborne acrylics can be extended by using additives like isopropanol or similar solvents in small quantities, nonionic surfactants, and neutralizing agents like ammonia for carboxylic acid groups. The type of surfactant used affects the stability of water based dispersions [36].

The use of halogenated acrylate monomers like dodecafluoroheptyl methacrylate or 2,2,2-trifluoroethyl methacrylate in the composition increases hydrophobic and oleophobic properties of coating film, and they induce protective performance. Such waterborne acrylates can be used in the protection of ancient stones [37,38]. The use of fluorine polymers such as poly(vinylidene fluoride) in acrylic coats improves the weathering resistance of opaque exterior acrylic coatings [39,40].

Another very useful application of fluorinated acrylics is in the manufacturing of antigraffiti coatings. The removal of graffiti is quite costly as the amount to be removed each time is very immense. Coatings with very low surface energy can ease the removal problem, and acrylic binders synthesized using fluorinated monomers can be used to make antigraffiti coatings. Water based acrylic binders synthesized using methyl methacrylate, butyl methacrylate, and trifluoroethyl methacrylate can be used for this purpose with a total fluorine content of only 1–2%. The fluorine components migrate to the surface of the coating and drastically reduce the adhesion of foreign materials [41].

11.8.1. Hybrid Coatings

The creation of inorganic domains in the polymer can impart distinct properties. Hybrid coatings with inorganic and organic components can be prepared by using tetraethyl orthosilicate (TEOS). A waterborne acrylic having 2-hydroxyethyl methacrylate at the backbone can be used to make hybrid coatings. The waterborne acrylate copolymer, TEOS, and surfactant like sodium lauryl ether sulfate are dissolved in tetrahydrofuran and the mixture is refluxed for about 1 hour. TEOS hy-

drolyzes and condenses with the hydroxyl groups of 2-hydroxyethyl methacrylate. Thus, the inorganic hybrid phase forms chemical bonds with organic phase, and a kind of interpenetrating polymer system forms [42]. The inorganic base increases the mechanical strength and the thermal stability of the coating film.

Polyacrylate/silica hybrid latexes with high silica content can be prepared by the direct mixing of colloidal silica up to about 20% and also silane agents, notably 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, and 3-aminopropyltriethoxysilane, with polyacrylate emulsion. The sol-gel reactions take place within 2 days at room temperature after casting the film. It can be then annealed at 80°C for 12 hours. The cosolvents like ethanol, isopropanol, and isobutanol improve surface appearance [43].

The acrylic emulsions used for exterior coating materials must have good stain resistance. The organic silane hybridized acrylic resin emulsion shows better stain resistance than conventional acrylic resin emulsion. The performance can be further improved by adding colloidal silica (with particle size ~ 7.5 nm) that increases the hydrophilicity of the coating film, and coatings with excellent stain resistance can be prepared [44].

Acrylic polyol resins can be modified with silicone resins by mixing them at varying fractions and allowing them to dry at ambient temperature. The mechanical properties show an increasing tendency up to 30% silicone content, but the T_g keeps increasing with the further increase in the fraction of silicone resin [45].

Alkoxysilane functionalized latexes can self cross link at ambient temperatures through alkoxysilane groups and form coating films with superior properties. However, the silane moieties can start up early hydrolysis and condensation reactions during polymerization and storage, and the coating film may not achieve its maximum mechanical properties. This adverse effect can be minimized by doing the polymerization via miniemulsion technique [46,47]. In this system, the monomers do not need to leave the droplet and thus they do not contact water. The composition of monomer mixture affects the stability of the droplet. No coagulations occur when the mixtures butyl acrylate (BA)/3-methacryoxypropyltrimethoxysilane (MPMS), BA-methyl methacrylate (MMA)/MPMS, and BA-styrene (St)/MPMS are used in miniemulsion polymerization [48]. So BA/St/MPMS mixture can safely be used to make hybrid coatings. The monomers are mixed with an initiator and a stabilizer like hexadecane and are introduced into wa-

ter having sodium lauryl sulfate as a surfactant. After stirring for 10 minutes, it is ultrasonicated for 3 minutes to obtain miniemulsion. The copolymerization is done at 70°C within three hours [49]. The hydrolysis and condensation of silane groups establishes a network structure between acrylic chains. The hydrolysis of alkoxy silane occurs in an acidic or basic media; therefore, the pH of the medium should be well controlled. At pH = 5.5 the gel content reaches 92% but cracks form in the film; however at pH = 7.5 and 8.5, the gel content becomes 72% and 86%, respectively, and homogeneous and transparent films form [49]. The incorporation of triethoxyvinylsilane to vinylacetate-acrylic emulsions increases the particle size and the heat stability, but the T_g decreases. The silane molecule in the chain converts the thermoplastic structure to an elastomeric structure due to sol-gel reactions. It also decreases the polymerization reaction rate, but the rate can be increased by increasing the concentration of initiator [50].

Surface modified silica can be introduced to acrylic-polyol and butylated melamine-formaldehyde based resins to increase scratch resistance in automotive clear coatings. Surface modification can be carried out by using hydrophobic silanes like methacrylsilane, hexamethyldisilane, and dimethyldichlorosilane. The nanosilica particles decrease activation energy for curing reactions [51].

Silicone containing acrylic monomers can be used to make versatile coating materials containing both silicon and other inorganic materials like montmorillonite nanoclay. The coating film offers faster drying speed, smaller surface tension, and improved water resistance [52].

Hybrid coatings can be produced also from poly(vinyl alcohol) and nanoclay. The sodium cloisite clay is first exfoliated by L-tyrosine amino acid by vigorously mixing it at 40°C for 3 hours, and then sonicating it for 30 minutes. Zinc oxide nanoparticles can be also added to improve the properties of the coating film. The mixture is stirred for 6 hours at 90°C. Zinc oxide increases thermal stability of the films and offers UV shielding as zinc oxide strongly absorbs UV radiation.

The titania nanoparticles with hydroxyl groups on the surface reacts with aminosilanes like 3-aminopropyltriethoxy silane, giving amino functionalized particles. The grafting occurs via the reaction between the hydroxyl groups of the nanoparticles with the ethoxy groups of silane molecules. These functionalized particles can be added into poly(vinyl alcohol) (PVA) and emulsified by sonication for 2 hours. The amino groups on the nanoparticles make hydrogen bonding with the hydroxyl groups of PVA reducing the settling of titania particles.

Titania absorbs UV radiation and thus it can be used to shield against UV light [53].

The aqueous dispersion of colloidal silica with a particle size of 15–30 nm can be added to PVA to improve the properties in general. The film shows superior mechanical properties, higher dissolution resistance in boiling water, and lower permeability [54].

Statues and architectural elements can be protected by polyacrylates like copoly(methyl acrylate/ethyl methacrylate) [55]. In order to improve the protection, a two-layer coating may be applied, one solvent based primer and the other waterborne topcoat which contains poly(vinylidene fluoride). The performance of the two-layer coating is further improved by annealing at 60°C [56].

The organic-inorganic hybrids can be prepared by in situ minemulsion polymerization of acrylic monomers in the presence of colloidal silica. The polymer film surrounds each nanoparticle as a shell. The gloss comes out to be low but it exhibits high flame resistance [57].

11.8.2. Core-Shell Acrylics

In order to improve the physical and mechanical properties of acrylic resins, they can be blended with other resins, copolymerized with special monomers and macromonomers, or hybridized with other polymers. Another method to enhance the properties is to prepare core-shell polymers. Acrylic polymers do not have high wear resistance, and this bears a series of problems when used in traffic paints. In many countries solvent based traffic paints are not preferred and eco-friendly water based traffic paints are used, and most of them are made from acrylic emulsions. Besides the poor wear resistance, it may take several hours for acrylic emulsions to dry in humid weather. The properties of acrylic coatings can be improved by core-shell systems [58].

In core-shell polymers, a second polymer with different physical and mechanical properties polymerizes on another polymer which acts as a core polymer. The core-shell particles have at least two kinds of properties exhibited by the core and by the shell material, such as two different T_g s. The interphase materials may also exhibit a different property.

A core-shell acrylate polymer with a soft core and hard shell can be prepared using n-butyl acrylate in the core and methyl methacrylate in the shell. The preparation of core-shell polymers starts with the synthesis of a seed lattice using the core monomers. About one-third of the core monomer is emulsion polymerized to synthesize the seed polymer.

Then the remaining monomer is gradually added into reactor in 1–2 hours at around 80°C. Once the synthesis of the core is over, the shell monomer is added slowly into the reactor in 2 hours [59]. Other monomers may also be introduced to modify the properties, and copoly(n-butyl acrylate/methacrylic acid/ethylene glycol dimethylacrylate) can be used as core, and copoly(styrene/methyl methacrylate) as shell [60]. Another soft core shell structure can be prepared by using styrene-butyl acrylate-acrylic acid as core and methyl methacrylate-acrylic acid as the shell [61]. The use of fluorinated acrylate monomer in the shell increases water repellency and thermal stability of the core-shell polymer [62].

The core and shell polymers may be quite different from each other. For instance, an oil based polyurethane can be used as a core and styrene-butyl acrylate copolymer as the shell [63]. In general, alkyd resins, polyesters, epoxy resins, and polyurethanes can be used as core [64]. Polymers with inorganic components like siliconated urethane may be used as shell polymer. Silicone polyurethanes have superior flexibility, thermal stability, resistance to humidity, and resistance to solvents and chemicals, but they have low oil resistance. In order to increase the environmental stability, fluorinated polymers which are water and oil repellent must be used in coatings. Since fluorinated polymers are expensive materials they can be combined with siliconized polymers in surface coating. Silicone and fluorine can both be introduced into coating by core-shell polymers. An acrylate monomer mixture containing fluorinated acrylate can be polymerized around a siliconized urethane core to prepare a core-shell polymer. Butyl acrylate and 2,2,2-trifluoroethyl methacrylate can be used for this purpose [65]. The use of fluorinated acrylates only in the shell reduces the cost, and from this point of view, the use of core-shell polymers is much more economical than using traditional emulsion acrylate systems for special purpose coatings [66]. Core-shell polymers are two-phase systems and can have better mechanical properties than other types of polymer systems. In fact, a polyurethane-polyacrylate core-shell polymer has better mechanical properties than their interpenetrating form [67].

Core-shell polymers with acrylic cores and siloxane in the shell can be prepared by polymerizing the siloxanes around the core. A mixture of butyl acrylate, methyl methacrylate, trihydroxymethylpropane triacrylate and 3-methacryloxypropyl trimethoxysilane can be used in the core, and a hexamethyldisiloxane in the shell. After preparing the seed polymer, the core is prepared by using the remaining acrylate mono-

mers and also 3-methacryloxypropyl trimethoxysilane. Then hexamethyldisiloxane is introduced slowly. A residual amount of octamethylcyclotetrasiloxane may also be added [68].

In multiphase latex, particle phase separation may occur. The morphology of such systems is controlled by both kinetic and thermodynamic factors [69]. The interfacial energies result in the driving forces that are responsible for thermodynamic factors. The kinetic factors are due to chain diffusion because of radical penetration, polymer phase separation, and phase combination. If the equilibrium is achieved by core-shell morphology, it will be easy to achieve. If the system achieves equilibrium by inverted core-shell, the spherical particles will be distorted and non-spherical particles are likely to occur. The equilibrium is easily achieved only if the polymer chains have high mobility [69].

The controlled modification of properties can be achieved by preparing multi-layer core-shell polymers [70]. It gives higher flexibility to change the type and the fraction of monomers. Another system is gradient emulsion polymerization, where the concentration of one of the monomers in the mixture is changed in time. In other words, acrylic latex formation is started with a certain monomer composition but one of the monomers is added gradually in time. For instance, if butyl acrylate is added gradually in a butyl acrylate-methyl methacrylate system, the final latex particle becomes rich in butyl acrylate content on the surface and the surface becomes softer than the central part. If methyl methacrylate is gradually added, the surface becomes harder than the central part. The polymerization can be carried out in a series of continuously stirred tank reactors (CSTR) for continuous production [71].

11.9. REFERENCES

1. H. Satapathy and A.K. Banthia, *Pigm. Resin Technol.*, 37(1) (2008) 21–27.
2. V.C. Malshe and N.S. Sangaj, *Prog. Org. Coat.*, 53 (2005) 207–211.
3. J. Branquinho, J.A.C. Alves, S. Carvalho, J. Moniz, F.a. Oliveira, and M.H. Gil, *J. Coat. Technol. Res.*, 6(4) (2009) 483–491.
4. M.D. Soucek and E. Pedraza, *J. Coat. Technol. Res.*, 6(1) (2009) 27–36.
5. C.G. Koukiotis, M.M. Karabela, and I.D. Sideridou, *Prog. Org. Coat.*, 75 (2012) 106–115.
6. N. Kessel, D.R. Illsley, and J.L. Keddie, *J. Coat. Technol. Res.*, 5(3) (2008) 285–297.
7. R.G. Joshi, T. Provder, P. Ziemer, W. Mao, W. Shen, and F.N. Jones, *J. Coat. Technol. Res.*, 6(1) (2009) 47–65.
8. W.A.E. Dunk, Binders for Waterborne Coatings, in *The Chemistry and Physics of Coatings*, ed: A. Marrion, The Royal Society of Chemistry, Cambridge, 2004.
9. L.X. Hien, D.T.N. Minh, N.T.V. Trieu, and C. Decker, *J. Coat. Technol. Res.*, 8(3) (2011) 343–353.

10. H.Y. Erbil, Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers, CRC Press, 2000.
11. S. Tıǧlı and V. Evren, *Prog. Org. Coat.*, **52** (2005) 144–150.
12. C. Koukiotis and I.D. Sideridou, *Prog. Org. Coat.*, **69** (2010) 504–509.
13. H. Berber, A. Sarac, and H. Yildirim, *Prog. Org. Coat.*, **71** (2011) 225–233.
14. D. Fukuhara and D. Sundberg, *JCT Research*, **2**(7) (2005) 509–516.
15. D.M. Mahli, J.M. Wegner, J.E. Glass, and D.G. Phillips, *JCT Research*, **2**(8) (2005) 627–634.
16. D.M. Mahli, J.M. Wegner, J.E. Glass, and D.G. Phillips, *JCT Research*, **2**(8) (2005) 635–647.
17. F. Ferrero and G. Malucelli, *Prog. Org. Coat.*, **53** (2005) 246–255.
18. L.N. Butler, C.M. Fellows, and R.G. Gilbert, *Prog. Org. Coat.*, **53** (2005) 112–118.
19. C.L. Zhao, S. Porzio, A. Smith, H. Ge, H.T. Davis, and L.E. Scriven, *JCT Research*, **3**(2) (2006) 109–115.
20. J.L. Keddie and A.F. Routh, *Fundamentals of Latex Film Formation*, Springer, 2010.
21. K.W. McCreight, R. Stockl, C. Testa, and K.S. Seo, *Prog. Org. Coat.*, **72** (2011) 102–108.
22. S. Ugur, A. Alemdar, and Ö. Pekcan, *JCT Research*, **2**(7) (2005) 565–575.
23. Z. Zong, S. Wall, Y.Z. Li, J. Ruiz, H. Adam, C. Badre, and F. Trezzi, *Prog. Org. Coat.*, **72** (2011) 115–119.
24. I. Mussard, Practical Aspects of Formulating with Associative Thickeners, in *Additives in Water-borne Coatings*, The Royal Society of Chemistry, ed: G. Davison and B. Lane, The Royal Society of Chemistry, Cambridge, 2003.
25. J. Bieleman, *Additives for Coatings*, Wiley-VCH Verlag, 2000.
26. M. Taheran, A.H. Navarchian, and R.S. Razavi, *Prog. Org. Coat.*, **72** (2011) 486–491.
27. T. Wada, T. Uragami, and Y. Matoba, *JCT Research*, **2**(8) (2005) 577–582.
28. M.B. Stroisz nigg, G.M. Wallner, B. Strauß, L. Jandel, and R.W. Lang, *Prog. Org. Coat.*, **65** (2009) 328–332.
29. J.M.R. Fernández, C. Guillem, A.L. Buendía, M. Paulis, and J.M. Asua, *Prog. Org. Coat.*, **72** (2011) 438–442.
30. S. Fatemi, M.K. Varkani, Z. Ranjbar, and S. Bastani, *Prog. Org. Coat.*, **55** (2006) 337–344.
31. R.M. Wang, J.F. Wang, X.W. Wang, Y.F. He, Y.F. Zhu, and M.L. Jiang, *Prog. Org. Coat.*, **71** (2011) 369–375.
32. V. Kumthekar and S. Kolekar, *Prog. Org. Coat.*, **72** (2011) 380–386.
33. F.N. Jones, W. Mao, P.D. Ziemer, F. Xiao, J. Hayes, and M. Golden, *Prog. Org. Coat.*, **52** (2005) 9–20.
34. G. Ahmetli, H. Deveci, A. Altun, and R. Kurbanli, *Prog. Org. Coat.*, **70** (2011) 9–15.
35. M.P. Oliveira, C.R. Silva, and L.M. Guerrini, *J. Coat. Technol. Res.*, **8**(4) (2011) 439–447.
36. E. Makarewicz and J. Kowalik, *Prog. Org. Coat.*, **49** (2004) 115–124.
37. L. He, J. Liang, X. Zhao, W. Li, and H. Luo, *Prog. Org. Coat.*, **69** (2010) 352–358.
38. E. Alyamac, M.D. Soucek, *Prog. Org. Coat.*, **71** (2011) 213–224.
39. V. Landry and P. Blanchet, *Prog. Org. Coat.*, **75** (2012) 494–501.
40. K. Wood, *Macromol. Symp.*, **187** (2002) 469–479.
41. J. Scheerder, N. Visscher, T. Nabuurs, and A. Overbeek, *JCT Research*, **2**(8) (2005) 627–625.
42. H.J. Naghash, A.R. Massah, and M. Arman, *Prog. Org. Coat.*, **65** (2009) 275–280.
43. W. Liao, H. Teng, J. Qu, and T. Masuda, *Prog. Org. Coat.*, **71** (2011) 376–383.
44. T. Wada and T. Uragami, *JCT Research*, **3**(4) (2006) 267–274.
45. B. Vengadaesvaran, S.R. Rau, K. Ramesh, R. Puteh, and A.K. Arof, *Pigm. Resin Technol.*, **39**(5) (2010) 283–287.

46. J.M.R. Fernández, Ir. Belena, M.D.R. Sánchez, M. Fuensanta, C. Guillem, and A.M.L. Buendia, *Prog. Org. Coat.*, 75 (2012) 86–91.
47. A.M. Herk and K. in *Hybrid Latex Particles*, Springer, 2010.
48. Y. Luo, H. Xu, and B. Zhu, *Polymer*, 47 (2006) 4959–4966.
49. S.W. Zhang, R. Liu, J.Q. Jiang, and H.Y. Bai, *Prog. Org. Coat.*, 65 (2009) 56–61.
50. H.J. Naghash, S.R. Mallakpour, and N. Mokhtarian, *Prog. Org. Coat.*, 55 (2006) 375–381.
51. Z. Ranjbara, A. Jannesari, S. Rastegar, and S. Montazeri, *Prog. Org. Coat.*, 66 (2009) 372–376.
52. H.J. Naghash and R. Mohammadrahimpanah, *Prog. Org. Coat.*, 70 (2011) 32–38.
53. S. Mallakpour and A. Barati, *Prog. Org. Coat.*, 71 (2011) 391–398.
54. M. Sarkar and P. Deb, *Adv. Polym. Technol.*, 27(3) (2008) 152–162.
55. M.K. Khallaf, A.A. Midany, and S.E. Mofty, *Prog. Org. Coat.*, 72 (2011) 592–598.
56. N.A. Swartz, K.A. Wood, and T.L. Clare, *Prog. Org. Coat.*, 75 (2012) 215–223.
57. T. Mizutani, K. Arai, M. Miyamoto, and Y. Kimura, *Prog. Org. Coat.*, 55 (2006) 276–283.
58. D. Sun and Y. Zhang, *J. Coat. Technol. Res.*, 9(2) (2012) 151–156.
59. G.J. Wang, C.S. Kang, and R.G. Jin, *Prog. Org. Coat.*, 50 (2004) 55–61.
60. L.J. Borthakur, T. Jana, and S.K. Dolui, *J. Coat. Technol. Res.*, 7(6) (2010) 765–772.
61. A.K. Khan, B.C. Ray, J. Maiti, and S.K. Dolui, *Pigm. Resin Technol.*, 38(3) (2009) 159–164.
62. G. Xu, L. Deng, X. Wen, P. Pi, D. Zheng, J. Cheng, and Z. Yang, *J. Coat. Technol. Res.*, 8(3) (2011) 401–407.
63. Y. Lu, Y. Xia, and R.C. Larock, *Prog. Org. Coat.*, 71 (2011) 336–342.
64. A. Guyot, K. Landfester, F.J. Schork, and C. Wang, *Prog. Polym. Sci.*, 32 (2007) 1439–1461.
65. J. Dai, X.Y. Zhang, J. Chao, and C.Y. Bai, *J. Coat. Technol. Res.*, 4(3) (2007) 283–287.
66. Z. Qin and W. Tu, *Pigm. Resin Technol.*, 39(1) (2010) 36–41.
67. V.D. Athawale and M.A. Kulkarni, *Pigm. Resin Technol.*, 39(3) (2010) 141–148.
68. B.L. Liu, B.T. Zhang, S.S. Cao, X.B. Deng, X. Hou, and H. Chen, *Prog. Org. Coat.*, 61 (2008) 21–27.
69. J.M. Stubbs and D.C. Sundberg, *Prog. Org. Coat.*, 61 (2008) 156–165.
70. C. Xu, T. Qiu, J. Deng, Y. Meng, L. He, and X. Li, *Prog. Org. Coat.*, 74 (2012) 233–239.
71. X. Zhang, X. Wei, W. Yang, Y. Li, and H. Chen, *J. Coat. Technol. Res.*, 9(6) (2012) 765–774.