CELLOSIZE
HYDROXYETHYL CELLULOSE
For Emulsion Polymerization
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Synthetic latices are extensively used as binders in paints, adhesives, paper, textile and various other end-applications. They can be characterized as aqueous dispersions of polymer particles produced by a chemical process known as emulsion polymerization. In this process, monomers are converted into polymers in an aqueous emulsion system in the presence of emulsion stabilizers and catalyzed by water-soluble radical initiators.

Latices offer a unique combination of interesting physical properties. They are low viscosity polymer systems which are used in water-borne, environmentally friendly systems. Stability and rheology dominate the physical properties required for most applications.

Latices should remain colloidally stable when stored over a long period, when subjected to shear forces or when incorporated into a formulation. In the presence of other formulation ingredients, the latex stability should be maintained. When latices are destabilized, coagulation or agglomeration of the polymer particles occurs which can be accompanied with layering of the system. This will have a negative impact on the performance of the latex and, therefore, stability is of utmost importance. This stability is obtained largely from the stabilizer system used in the manufacturing of the latex.

Each application requires a certain rheology of the binder-latex. In some cases, good flow after application is required in semigloss emulsion paints where brush or roller marks must be leveled out, while in other cases flow of the formulation after application must be avoided in some special textile applications. The required flow properties can usually be obtained by control of particle size and particle size distribution of the latex. For a given polymerization process or technique, the particle properties are strongly influenced by the type and level of the stabilizer system.

CELLOSIZE Hydroxyethyl Cellulose: A Protective Colloid for Emulsion Polymerization

Introduction

Synthetic latices are extensively used as binders in paints, adhesives, paper, textile and various other end-applications. They can be characterized as aqueous dispersions of polymer particles produced by a chemical process known as emulsion polymerization. In this process, monomers are converted into polymers in an aqueous emulsion system in the presence of emulsion stabilizers and catalyzed by water-soluble radical initiators.

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CELLOSIZE hydroxyethyl cellulose (HEC) can be used as part of the latex stabilizer system where it acts as a protective colloid. In this respect CELLOSIZE HEC will contribute to both stability and rheology of the system. CELLOSIZE HEC is available in a wide range of grades, allowing the customer to select the appropriate protective colloid for any given application requirement of stability and rheology. The narrow specification limits of the various CELLOSIZE HEC grades offer a highly reproducible and reliable product needed for the production of emulsion polymers.
Latex Types

Emulsion polymers are normally classified based on the monomer(s) used in their production. The basic monomer composition determines primarily the abrasion resistance, the water adsorption, and the minimum film forming temperature (MFFT) of the latex. Monomers are classified based on the hardness of their homopolymer.

- Monomers producing rubber-like polymers are called “soft monomers.” Examples of these include acrylates, butadiene, ethylene and vinyl versatate.
- Monomers producing glass-like polymers are called “hard monomers.” Examples of these include methacrylates, vinyl acetate, styrene and vinyl chloride.

To obtain optimal film building properties at a given temperature, combinations of hard and soft monomers are frequently used. The soft monomer functions as an internal plasticizer. If only hard monomers are used, like in poly(vinyl acetate) latices, an external plasticizer like n-butyl phthalate must be added to obtain good film building.

Typical industrial latices are presented in Table 1. Hydroxyethyl cellulose is extensively used in the polymerization of vinyl homopolymers and vinyl copolymers, including vinyl-acrylics. To some extent it is also used in the polymerization of all-acrylics.

Table 1: Classification of common latex types

<table>
<thead>
<tr>
<th>Latex type</th>
<th>Main applications</th>
<th>Use of HEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylated styrene - butadiene (SBR) latex</td>
<td>Textile, Paper, Adhesives</td>
<td>–</td>
</tr>
<tr>
<td>Vinyl acetate homopolymer</td>
<td>Adhesives, Construction</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl acetate copolymer (with acrylates, vinyl versatate, maleates, fumarates)</td>
<td>Paint</td>
<td>++</td>
</tr>
<tr>
<td>Methyl methacrylate-acrylate copolymers</td>
<td>Paint</td>
<td>+</td>
</tr>
<tr>
<td>Styrene - acrylics</td>
<td>Paint</td>
<td>–</td>
</tr>
<tr>
<td>Vinyl acetate - ethylene - vinyl chloride (pressure polymers)</td>
<td>Paint</td>
<td>++</td>
</tr>
</tbody>
</table>

++ Very frequent use  
+ Frequent use  
– Normally not used

† Vinyl versatate refers to the vinyl ester of versatic 10 acid (vinyl neodecanoate, CAS 5100-52-3)
Latex Manufacturing Techniques

There are basically four different techniques to produce latices: the semi-batch process, the full batch process, the staged adiabatic or shot process and the continuous process.

The most important industrial manufacturing technique is the **semi-batch process**. Most of the water used in the batch is charged initially. The stabilizer system, buffer, and other miscellaneous components are added and dissolved in the water. Subsequently, some initial monomer (5-10%) is charged and the mixture is then heated to the reaction temperature. Initial catalyst (radical initiator) is fed in to start the pre-polymerization (seeding). After the exothermic reaction has ceased, the remaining monomer(s) is fed to the reactor at such a rate that the heat generation is controlled. The reaction is conducted at a constant temperature.

There are many variations of the semi-batch process. For instance, a catalyst stream and/or a stabilizer solution may be fed along with the monomer. The monomer can also be added as an aqueous emulsified monomer-system (emulsion addition technique). The key process technique involved in the semi-batch process, however, is the delayed monomer addition which permits easy control over the polymerization rate, polymerization temperature, the copolymer composition, particle size and polymer molecular weight.

In the **full batch process**, the catalyst is added when all the ingredients have been charged to the reactor. In this process, all monomers are present from the beginning of the polymerization. The **staged adiabatic or shot process** is derived from the batch process in which the monomers are added in different “shots.” The process is mainly used for redox initiated polymerizations at modest temperature.

The **continuous process** is carried out in a series of connected stirred-tank reactors where the recipe ingredients are supplied to the first tank and the final product is removed from the last tank.

Stabilization of Emulsion Polymers

To stabilize the polymer particles in the continuous aqueous phase, the particles must be sheathed by a transitional layer which prevents the particles from agglomerating. Two stabilization mechanisms can be distinguished:

a. Electrostatic stabilization: This stabilization arises from ionic groups, present at the surface of the particle, which repel each other. These ionic groups can be anionic surfactants, (e.g., alkyl or aryl sulfates or sulfonates); anionic end-groups (e.g., sulfates from persulfate catalysts or anion-containing monomers such as carboxylic or sulfonic acid monomers).

b. Steric stabilization: This stabilization arises from bulky groups present at the surface of the polymer particles. These groups can be polymeric surfactants or protective colloids like CELLOSIZE hydroxyethyl cellulose.

In most latex-systems, stabilization is obtained by a combination of the two basic stabilization mechanisms described above. This is achieved by using as stabilizer-system a combination of anionic and nonionic surfactants next to a hydrophilic polymer acting as a protective colloid.
The Role of CELLOSIZE HEC as a Protective Colloid

Figure 1: The structure of hydroxyethyl cellulose (idealized)

To gain some insight into how CELLOSIZE hydroxyethyl cellulose (HEC) acts as a protective colloid around the polymer particles, the structure of HEC (Figure 1) should be considered. Under emulsion polymerization conditions, free radicals are produced to initiate the polymerization. These radicals can induce free radical sites on the hydroxyethyl cellulose backbone by hydrogen abstraction of the acetal hydrogen (see Scheme 1). These reactive sites can initiate the emulsion polymerization of the monomers. By this reaction sequence, the hydroxyethyl cellulose becomes chemically bonded onto the formed polymer. The protective colloid is in this case firmly and irreversibly grafted onto the polymer surface which gives an optimal protective colloid action. If this grafting reaction does not occur, there is the possibility for the hydroxyethyl cellulose chain to adsorb onto the particle surface. This loosely reversible physical adsorption leads, however, to an inferior protective colloid action.

To visualize the action of CELLOSIZE HEC in an emulsion polymerization process, the following description is helpful (see Scheme 2, Harkins’ Theory). In the initial polymerization mixture (see Step 1–initial mixture), the monomers are present as large surfactant-stabilized droplets in a continuous aqueous phase. Monomers used in emulsion polymerization have a limited solubility in water. The total level of surfactants is high enough to have surfactant micelles in the aqueous phase which can solubilize some monomers. The CELLOSIZE HEC is also present in the aqueous phase.

When the water-soluble initiator is added (Step 2–latex particle nucleation), the polymerization starts in the micelles where monomer is present. The initiator also forms radicals with the monomers and the protective colloid present in the aqueous phase. The protective colloid radicals migrate to the micelles where they are grafted onto the growing polymer. The polymerization continues because monomers diffuse continuously from the large monomer droplets into the aqueous phase where they are adsorbed onto the growing polymer particles (Step 3–growth of polymer particles by adsorption of monomer). The polymerization in each monomer-swollen particle continues until the monomer droplets are depleted and no monomer and/or initiator is left (Step 4–polymerization in monomer-swollen polymer particles).

The protective colloid action of CELLOSIZE HEC in the final latex is presented in Figure 2. The water molecules surrounding the polymer particles are “bound” onto the surface due to the hydrophilic nature of the HEC chains. The polar end groups of the polymer, polar monomer segments, as well as polar surfactant species also contribute in binding part of the aqueous phase onto the polymer particles.

The “bound” water provides a transition between the hydrophobic polymer phase and the “free” or normal water in the continuous phase. This sheath or transitional layer provides the stability to the colloidal system. This type of stabilization is referred to as steric stabilization. The size of the polymer particles, coupled with the transitional layer, largely determines the rheological properties of the system. For example, the viscosity of the system can be considered as a measure of the balance between the volume fraction of polymer particle and “bound” water on one hand and “free” water on the other. Of course, the “bound” and “free” water are in a state of dynamic equilibrium.
Scheme 1: Grafting of hydroxyethyl cellulose onto the latex polymer

Free radical initiator

CH₂=CHX

• CHX-CH₂(CHX-CH₂)ₙ
Scheme 2: Emulsion polymerization process (Harkins’ Theory)

Step 1: Initial mixture

Step 2: Latex particle nucleation

Step 3: Growth of polymer particles by adsorption on monomer

Step 4: Polymerization in monomer-swollen polymer particles
Figure 2: Dynamic equilibrium of “bound” and “free” water
Chemistry of CELLOSIZE HEC in Emulsion Polymerization

The grafting of hydroxyethyl cellulose (HEC) onto the polymer particles is not the only reaction occurring during emulsion polymerization. Next to grafting, the cellulosic backbone will be cleaved to some extent, leading to smaller molecular weight HEC fragments. A general reaction pattern in which degradation and grafting are competitive reactions has been proposed. In Scheme 3, this pattern is presented with persulfate as the initiator. The radical HEC intermediate is the common intermediate for both grafting and degradation. The two possible reaction routes will normally occur simultaneously; however, either grafting or degradation will be favored depending on the reactivity of the monomer and the chemical structure of the HEC.

Vinyl monomers such as vinyl acetate or vinyl versatate have a relatively low reactivity toward radical intermediates. Therefore, HEC radicals generated in the presence of vinyl monomers will prefer the degradation route. Normally only 15% to 25% of the protective colloid is grafted in vinylic polymers.

Acrylic monomers like methyl methacrylate, butyl acrylate or 2-ethylhexyl acrylate are very reactive toward radical intermediates and the grafting reaction route is predominant in these systems. The different reaction paths of hydroxyethyl cellulose with vinylic versus acrylic systems will also give rise to different chemical and structural requirements of the CELLOSIZE HEC as a protective colloid.

Scheme 3: Proposed scheme of HEC reaction chemistry under standard emulsion polymerization conditions
Hydroxyethyl Cellulose Characteristics

Because CELLOSIZE hydroxyethyl cellulose is used as a chemical reagent in emulsion polymerization, its chemical structure can profoundly affect its performance. The structure of hydroxyethyl cellulose is mainly characterized by molecular weight, molar substitution (MS) and degree of substitution (DS).

- As already discussed, the most important characteristics for HEC, in relation to the emulsion polymerization process, are the ethylene oxide MS and DS or fundamentally the “substitution pattern” of the ethylene oxide groups on the cellulose backbone. The molar substitution is defined as the average number of hydroxyethyl groups per anhydroglucose unit and this number is theoretically unlimited. However, for practical reasons, commercial low viscosity grades of HEC are usually not produced above an MS of 3.0. The degree of substitution is defined as the average number of substituted hydroxyl groups per anhydroglucose unit. This number is limited to a theoretical maximum of 3.0. For the idealized structure of HEC shown in Figure 1, the MS is 2.5 and the DS is 1.5.

- CELLOSIZE hydroxyethyl cellulose grades for emulsion polymerization are produced in an MS range of 1.8 to 2.7 and a corresponding DS of 0.8 to 1.4. As a general rule, high MS products are recommended for vinylics, while lower MS products are recommended for acrylics. The reason for this is that grades showing a high DS/MS ratio tend to favor the grafting route upon initiation (see Scheme 3).

- The molecular weight of hydroxyethyl cellulose is related to its viscosity development in aqueous solution. In Table 2, the viscosity limits of the CELLOSIZE hydroxyethyl cellulose grades are presented. The normal protective colloid grades are the lower molecular weight type such as the 09, 3, 300 and 4400 grades.

All CELLOSIZE hydroxyethyl cellulose grades have very narrow viscosity limits, or molecular weight distributions, necessary to obtain a good emulsion polymerization reproducibility.

- Most of the CELLOSIZE HEC grades are offered in a WP and a QP version. The designation WP and QP refers to the degree of retardation during dissolution in water. Like all water-soluble polymers, care must be taken to prevent lump and gel formation when HEC is dissolved in water. If gel or lump formation occurs, adverse effects on latex viscosity, stability and grit formation can result. These problems can be avoided by understanding those factors which control the dissolution characteristics of CELLOSIZE HEC.

CELLOSIZE HEC is surface-treated to have a retarded dissolution behavior, and this surface-treatment permits the powder to disperse easily before the process of swelling and dissolution starts. The time available to disperse the powder in the water before the onset of dissolution is called the hydration time. The hydration time is affected by pH and temperature. QP types are more retarded and show a substantially longer hydration time than WP types. EP types have an intermediate hydration time. High pH and/or high temperatures decrease the time between dispersion and the onset of dissolution of HEC in water (the hydration time).

Table 2: Viscosity ranges of CELLOSIZE HEC grades

<table>
<thead>
<tr>
<th>Grade</th>
<th>Concentration, % by weight (dry basis)</th>
<th>Solution viscosity Brookfield LVT, 25°C, mPa•s</th>
<th>Spindle</th>
<th>rpm</th>
<th>Typical molecular weight (M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QP 09</td>
<td>5</td>
<td>75-150</td>
<td>1</td>
<td>30</td>
<td>65,000</td>
</tr>
<tr>
<td>EP 09</td>
<td>5</td>
<td>90-160</td>
<td>1</td>
<td>30</td>
<td>65,000</td>
</tr>
<tr>
<td>QP 3L</td>
<td>5</td>
<td>215-282</td>
<td>2</td>
<td>60</td>
<td>75,000</td>
</tr>
<tr>
<td>QP 300</td>
<td>2</td>
<td>300-400</td>
<td>2</td>
<td>60</td>
<td>200,000</td>
</tr>
<tr>
<td>EP 300</td>
<td>2</td>
<td>250-400</td>
<td>2</td>
<td>60</td>
<td>200,000</td>
</tr>
<tr>
<td>WP 300</td>
<td>2</td>
<td>300-400</td>
<td>2</td>
<td>60</td>
<td>200,000</td>
</tr>
<tr>
<td>QP 4400H</td>
<td>2</td>
<td>4800-8000</td>
<td>4</td>
<td>60</td>
<td>475,000</td>
</tr>
</tbody>
</table>

\[1\] EP 09 and EP 300 are special CELLOSIZE HEC products, developed to enhance grafting in emulsion polymerization of vinylic systems.
Ideally, CELLOSIZE HEC should be added under conditions which lead to a good dispersion such as neutral to acidic pH and/or cold to ambient temperature. Rapid dissolution can be subsequently obtained by increasing pH by the addition of the buffer (e.g., sodium acetate, sodium bicarbonate, borax) and/or by raising the temperature.

- CELLOSIZE HEC is a water-soluble polymer with very narrow specifications on the amount of water-insolubles present in the polymer. Water-insoluble material can either be unreacted cellulosic fibers, overdried HEC or small gel-like particles. The level of water-insoluble material in CELLOSIZE HEC is controlled very closely to prevent the formation of grit (scrap) in the emulsion polymerization process.

- CELLOSIZE HEC contains a limited amount of residual salt and volatiles. The salt present in the product is sodium acetate which is a known buffering agent in the latex production process. The volatiles content of all CELLOSIZE HEC grades is kept within tight specifications during production and packaging. However, as hydroxyethyl cellulose is a hygroscopic powder, it should be stored in closed containers to prevent adsorption of moisture. As packaged, the levels of salt and volatiles in CELLOSIZE HEC are controlled to ensure that the percentage of active polymer does not vary significantly between batches.

**CELLOSIZE HEC in Polymerization of Vinyl Ester Monomers**

In this part, the performance of CELLOSIZE HEC in vinylic polymerization is discussed. Typical examples of these latices are vinyl acetate homopolymers, vinyl acetate - vinyl versatate copolymers and vinyl acetate - vinyl chloride - ethylene pressure terpolymers. As already indicated, hydroxyethyl cellulose undergoes preferential degradation in these systems and only limited grafting occurs. The severe degradation of hydroxyethyl cellulose is illustrated in Table 3, where the influence of CELLOSIZE HEC molecular weight on later viscosity in a persulfate-initiated standard vinyl acetate - vinyl versatate emulsion polymerization is presented. We have found that there is very little correlation between the viscosity of the protective colloid and the final latex viscosity in these particular systems. For all standard HEC grades, similar latex viscosities are obtained. Under these polymerization conditions, CELLOSIZE HEC is degraded to a constant molecular weight nearly independent from the starting molecular weight. Because high viscosity grades can lead to process problems, it is usually recommended to use a QP 300 or lower viscosity CELLOSIZE HEC grade.
Degradation and grafting reactions are of utmost importance to the final rheology and stability of the latex. These properties can be controlled by various factors:

- Level of protective colloid. In vinylic polymerizations, it is recommended to use a protective colloid level of 1% to 3% by weight relative to monomer. Increasing the level results in higher latex viscosities and better stabilizing effect. For acrylic systems, a lower level protective colloid is more appropriate (see next section).

- Addition of chain transfer agents. These additives reduce the formation of HEC polymer radicals, thereby suppressing both the oxidative degradation and the grafting reaction. Water-soluble chain transfer agents like triethanolamine (TEA) or 2-mercaptoethanol can be used. The effect of triethanolamine (TEA) present in an all-vinylic latex is shown in Table 4. An increased level of TEA results in a higher latex viscosity due to reduced degradation of HEC. However, in doing so, care must be taken not to affect the stability of the emulsion because the reduction of grafting can increase the level of grit formation.

### Table 3: Influence of molecular weight of CELLSIZE HEC on the final latex viscosity in a persulfate initiated vinyl acetate-vinyl versatate emulsion polymerization

<table>
<thead>
<tr>
<th>Protective colloid</th>
<th>Approximate molecular weight (Mₐ) of HEC</th>
<th>Average latex viscosity (Brookfield RVT, spindle #6, 50 rpm, 20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELLSIZE QP 300</td>
<td>200,000</td>
<td>2500 mPa•s</td>
</tr>
<tr>
<td>CELLSIZE QP 4400H</td>
<td>475,000</td>
<td>2400 mPa•s</td>
</tr>
<tr>
<td>CELLSIZE QP 15000H</td>
<td>850,000</td>
<td>2260 mPa•s</td>
</tr>
<tr>
<td>CELLSIZE QP 30000H</td>
<td>1,000,000</td>
<td>2600 mPa•s</td>
</tr>
</tbody>
</table>

† For formulation and typical properties, see Section C of the polymerization formulations section, p. 19.

<table>
<thead>
<tr>
<th>Protective colloid</th>
<th>TEA level (% by weight, based on monomers)</th>
<th>Latex viscosity</th>
<th>Grit level</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELLSIZE QP 300</td>
<td>—</td>
<td>2000 mPa•s</td>
<td>30 ppm</td>
</tr>
<tr>
<td>CELLSIZE QP 300</td>
<td>0.1%</td>
<td>2520 mPa•s</td>
<td>45 ppm</td>
</tr>
<tr>
<td>CELLSIZE QP 300</td>
<td>0.3%</td>
<td>3600 mPa•s</td>
<td>120 ppm</td>
</tr>
<tr>
<td>CELLSIZE QP 300</td>
<td>0.5%</td>
<td>3800 mPa•s</td>
<td>259 ppm</td>
</tr>
</tbody>
</table>

†† For formulation and typical properties, see Section C of the polymerization formulations section, p. 19.

- Process variables. Process variables known to have an effect on grafting and degradation of the HEC are:
  - seed-feed initiator balance
  - monomer feed rates
  - seed-feed HEC balance

The above techniques can be used to increase the viscosity and stability of all-vinylic latices. However, these techniques show serious limitations because special additives, higher products levels or special process techniques are needed and some of them reduce the grafting efficiency of the HEC, leading to a lower emulsion stability.
A better way to obtain vinylic latices, giving a higher latex viscosity and improved stability, is to use CELLOSIZE EP 300 or CELLOSIZE EP 09 as the protective colloid. These CELLOSIZE products are hydroxyethyl celluloses with a different chemical structure than the standard CELLOSIZE types. The different hydroxyethyl substitution pattern leads to a lower tendency for cleavage of the cellulosic backbone during polymerization and also promotes the grafting of the protective colloid onto the polymer particles. In this way, a firmly bound protective layer can be formed around the latex particles, imparting high viscosity and good stability of the emulsion. In Table 5, latex viscosities obtained with CELLOSIZE EP 300, CELLOSIZE QP 300 and the lower molecular weight CELLOSIZE EP 09 in a vinyl acetate - vinyl versatate emulsion polymerization are presented. The polymerization procedures are described in Sections C, D and E of the polymerization formulations section.

Three polymerization initiator systems have been considered: a thermal initiation with ammonium persulfate and two redox initiations using the system persulfate - metabisulfite and the system t-butyl hydroperoxide - sodium formaldehyde sulfoxylate (TBHP-SFS). Under all of these initiator systems, CELLOSIZE EP grades offer a higher latex viscosity compared to the equivalent standard CELLOSIZE QP type. As already indicated, in the case of thermal initiation of vinylic emulsion polymerization, the molecular weight of the CELLOSIZE HEC protective colloid has little impact on final latex viscosity. However, for polymerizations conducted with redox initiation, an important effect of the molecular weight of CELLOSIZE HEC on latex viscosity is observed. A lower molecular weight HEC leads to a lower latex viscosity (CELLOSIZE EP 09 versus CELLOSIZE EP 300). Next to the structure of the CELLOSIZE HEC protective colloid, this case demonstrates the important influence of the initiator system on latex viscosity.

Table 5: Latex viscosities of vinyl acetate - vinyl versatate copolymer (Brookfield RVT, spindle 6, 50 rpm, 20°C)

<table>
<thead>
<tr>
<th>Protective colloid</th>
<th>THERMAL ammonium persulfate</th>
<th>REDOX persulfate metabisulfite</th>
<th>REDOX t-butyl hydroperoxide sodium formaldehyde sulfoxylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELLOSIZE EP 300</td>
<td>3500 mPa-s</td>
<td>2000 mPa-s</td>
<td>&gt; 10,000 mPa-s</td>
</tr>
<tr>
<td>CELLOSIZE QP 300</td>
<td>2500 mPa-s</td>
<td>1300 mPa-s</td>
<td>5000 mPa-s</td>
</tr>
<tr>
<td>CELLOSIZE EP 09</td>
<td>2500 mPa-s</td>
<td>1000 mPa-s</td>
<td>7000 mPa-s</td>
</tr>
</tbody>
</table>
**CELLOSIZE HEC Polymerization of Acrylic Monomers**

In the polymerization of all-acrylic latices such as methyl methacrylate - butyl acrylate or 2-ethylhexyl acrylate - acrylic acid copolymers, hydroxyethyl cellulose undergoes extensive grafting reactions. When the polymerization conditions are not well controlled, the high degree of grafting can easily lead to latex particle bridging by grafting of one HEC chain onto multiple polymer particles. This leads to agglomeration of the latex during polymerization. As discussed above, the grafting reaction of HEC can be controlled in several ways. For acrylic systems, the following general recommendations can be given:

- A low molecular weight hydroxyethyl cellulose like CELLOSIZE EP 09 is preferred to prevent possible particle bridging (short chain protective colloid).
- A low molar substitution hydroxyethyl cellulose is recommended to reduce grafting tendency. Preferably the molar substitution should not be higher than 2.0.
- The concentration of hydroxyethyl cellulose should be minimized. A concentration maximum of 0.2% by weight of CELLOSIZE HEC based on the monomers is recommended.
- Preferably, hydroxyethyl cellulose should be added near the end or even after addition of the monomers to reduce excessive grafting.
- The addition of chain-transfer agents like triethanolamine, 2-mercaptoethanol or 1-dodecanethiol during polymerization can effectively control agglomeration.

The advantage of using CELLOSIZE HEC in all-acrylic latices is to make use of its good stabilizing capacity which allows for a reduction in the total amount of stabilizer ingredients (surfactants and protective colloid). This can lead to a significant reduction of the surfactant level, yielding a reduction in both raw material cost and water adsorption of the latex.

CELLOSIZE HEC can also be used effectively in the preparation of vinyl-acrylic copolymers like vinyl acetate - butyl acrylate or vinyl acetate - 2-ethylhexyl acrylate latices. In these cases, no straight recommendation on grade choice of CELLOSIZE HEC can be given because their properties range between pure vinylic and pure acrylic latices. In general, one can say that increasing the CELLOSIZE HEC concentration will impart higher viscosities and improve the stability. Higher viscosities can also be obtained by using higher HEC viscosity grades. In principle, all CELLOSIZE HEC protective colloid grades can be used in these systems, but laboratory or pilot plant tests will be required to assess the optimum stability and rheology at an acceptable protective colloid level.
Water Adsorption of Latex Films

An important property of latices used in coatings is a reduced tendency to adsorb water. A good water barrier property is required for exterior coatings to prevent surface corrosion to metal and water damage to wood, and to improve washability of interior coatings. The level of hydrophilic components like hydroxyethyl cellulose in the production of latices should therefore be minimized. Next to the level of hydroxyethyl cellulose, the chemical structure of HEC is also an important factor in the water adsorption of a latex film.

In Figure 3, the water adsorption of vinyl acetate-vinyl versatate latex films is plotted as a function of the molar substitution (MS) of the hydroxyethyl cellulose used as a protective colloid. An important increase in water adsorption is observed when the molar substitution is increased. Although the major determining factors in the water adsorption of a latex film are the monomer composition and level of stabilizers, the use of a hydroxyethyl cellulose with lower molar substitution is an advantage.

Figure 3: Water adsorption of vinyl acetate - vinyl versatate latex†

† Formulation: see Section C of the polymerization formulation section, p.19.

CELLOSIZE HEC as Part of the Total Stabilizing System

A typical stabilizing system used in vinylic emulsion polymerization consists of an anionic surfactant, a nonionic surfactant and a protective colloid. This system will make use of the synergy between electrostatic and steric stabilization to lead to an optimal stabilization performance under various conditions. The surfactants play an important role in the stabilization of the initial monomer emulsion and also in the nucleation of the polymer particles which occurs in the surfactant micelles. The protective colloid plays an important role in the stabilization of the final latex. In this light, CELLOSIZE HEC offers good storage and shear stability as well as an excellent freeze-thaw stability.
The components of the stabilizing system have an important influence on the particle size of the latex. Both nonionic surfactants and hydroxyethyl cellulose tend to impart a large particle size while anionic surfactants tend to induce a small particle size. Latices prepared with hydroxyethyl cellulose normally have an average latex particle size above 0.2 microns. The level of anionic surfactants has a high influence on latex particle size and viscosity. With an increasing level of anionic surfactant, the particle size decreases and the latex viscosity increases substantially. Good control over particle size is needed in emulsion polymerization because specific properties of the latex in an application are related to the particle size. In a paint system, for instance, small particle size latices will lead to a higher pigment binding capacity, but if the particle size becomes too small, the leveling performance of the paint will be impaired. Latices must therefore have a well defined particle size and this can be obtained by proper selection of the stabilizer system. CELLOSIZE HEC is an important aspect of the total stabilizing system.

**Emulsion Polymerization Formulations**

**A. Poly(Vinyl Acetate) Latex**

**A.1 Formulation (percent by weight)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>40.902 %</td>
</tr>
<tr>
<td>CELLOSIZE QP 4400H</td>
<td>1.0 %</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate (as 6.5% aqueous solution)</td>
<td>3.15 %</td>
</tr>
<tr>
<td>Nonylphenol (20) ethoxylate (as 80% aqueous solution)</td>
<td>0.48 %</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>0.074 %</td>
</tr>
<tr>
<td>Antifoam</td>
<td>0.004 %</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer: Vinyl acetate</td>
<td>50.8 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water</td>
<td>1.0 %</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>0.05 %</td>
</tr>
<tr>
<td>2. Water</td>
<td>2.0 %</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>0.03 %</td>
</tr>
<tr>
<td>3. Water</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>0.01 %</td>
</tr>
</tbody>
</table>

**A.2 Procedure**

1. Place the initial aqueous charge in the reactor.
2. Add 7.8% of the vinyl acetate and stir the mixture at 150 rpm.
3. Raise the temperature to 70°C and add catalyst mixture 1.
4. After 10 minutes, add the remaining monomer and catalyst mixture 2 over a period of three hours. Maintain the temperature of the reaction mixture at 75°C.
5. Add the catalyst mixture 3 and hold the latex at 75°C for one hour (cook-out period).
6. Cool the latex to room temperature.
A.3 Latex properties

Brookfield RVT viscosity
(50 rpm, spindle 5, 20°C) 2000 to 2500 mPa•s
pH 4.3 to 4.4
Solids content 52%
Grit level (200 mesh) 60 to 75 mg/kg

B. Poly(Vinyl Acetate) Latex

B.1 Formulation (percent by weight)

1. Initial charge:
   - Deionized water 41.30%
   - Sodium bicarbonate 0.05%
   - Sodium lauryl sulfate 0.25%
   - Octylphenol (40) ethoxylate 1.10%
   - CELLOSIZE QP 300 1.20%

2. Monomer charge:
   - Vinyl acetate 52.00%

3. Catalyst charge:
   - Ammonium persulfate 0.10%
   - Deionized water 4.00%

B.2 Procedure

1. Add 5% of the monomer and 20% of the catalyst charge to the reactor.
2. Prepolymerize the mixture at 75°C for 10 minutes.
3. Add the remaining monomer and catalyst over a period of 3 hours.
4. Postpolymerization at 75°C for one additional hour.

B.3 Latex properties

Brookfield LVT viscosity at 20°C (spindle 3)
At 12 rpm 5500 mPa•s
At 30 rpm 3500 mPa•s
At 60 rpm 3000 mPa•s
pH 4.6 to 4.8
Solids content 54 to 55%
Grit level (200 mesh) 20 to 40 mg/kg
C. Persulfate Initiated Vinyl Acetate - Vinyl Versatate Copolymer Latex

C.1 Formulation (percent by weight)

1. Initial charge:
   - Deionized water 42.0 %
   - CELLOSIZE EP 300 1.0 %
   - Sodium dodecylbenzene sulfonate (70% active, 10% aqueous solution) 2.8 %
   - Nonylphenol (20) ethoxylate (80% aqueous solution) 0.6 %
   - Sodium bicarbonate 0.076%
   - Antifoam 0.04 %

2. Monomer charge:
   - Vinyl acetate 34.8 %
   - Vinyl versatate 15.1 %

3. Initiator 1:
   - Deionized water 1.0 %
   - Ammonium persulfate 0.051%

4. Initiator 2:
   - Deionized water 2.0 %
   - Ammonium persulfate 0.031%

5. Initiator 3:
   - Deionized water 0.5 %
   - Ammonium persulfate 0.011%

C.2 Procedure

1. Charge the reactor with the initial charge. Adjust the reactor temperature control bath to 75°C and reactor stirrer speed to 150 rpm.
2. Add 7.8% of the monomer charge and adjust the temperature of the bath to 85°C.
3. When the temperature inside the reactor is stabilized, add initiator 1 and control the temperature of the mixture at 80°C.
4. After prepolymerizing for 10 minutes, start feeding in the remainder of the monomer charge and initiator 2 over a period of 3 hours.
5. When the addition is completed (after 3 hours), add initiator 3 and maintain the temperature at 80°C for 1 hour.
6. After this additional hour of cook-out, cool down and discharge the reactor.

C.3 Latex properties

- Brookfield RVT viscosity (50 rpm, spindle 5, 20°C): 3000 to 4000 mPa-s
- pH: 4.2 ± 0.1
- Solids content: 51%
- Grit level (200 mesh): 20 to 60 mg/kg
D. \( t \)-Butyl Hydroperoxide - Sodium Formaldehyde Sulfoxylate Initiated Vinyl Acetate - Vinyl Versatate Copolymer Latex

D.1 Formulation (percent by weight)

1. Initial charge:
   - Deionized water \( 41.95\% \)
   - CELLOSIZE WP 300 \( 1.0\% \)
   - Nonylphenol (20) ethoxylate (80% aqueous solution) \( 0.61\% \)
   - Sodium dodecylbenzene sulfonate (10% aqueous solution) \( 2.8\% \)
   - Antifoam \( 0.04\% \)

2. Initiator system:
   a. TBHP emulsion
      - Deionized water \( 1.72\% \)
      - \( t \)-Butyl hydroperoxide (TBHP) \( 0.27\% \)
      - Sodium dodecylbenzene sulfonate \( 0.01\% \)
   b. SFS solution:
      - Deionized water (pH 5) \( 1.82\% \)
      - Sodium formaldehyde sulfoxylate (SFS) \( 0.18\% \)

3. Monomer mixture:
   - Vinyl acetate \( 34.6\% \)
   - Vinyl versatate \( 15.0\% \)

D.2 Procedure

1. Place the initial charge and 8% of monomer mixture in the reactor.
2. Heat the reactor content to 60°C.
3. Add 25% of the TBHP emulsion (a) and 25% of the SFS solution (b).
4. Hold the reactor at 60°C for 10 minutes.
5. Charge the remaining monomer mixture, TBHP emulsion and SFS solution to the reactor over a period of 3 hours at 60°C.
6. After the addition of the monomer mixture is complete, hold at 60°C for one hour.
7. Cool down to ambient temperature and discharge reactor.

D.3 Latex properties

- Brookfield RVT viscosity (50 rpm, spindle 5, 20°C) \( 4500\) to \( 5000\) mPa•s
- pH \( 4.8\) to \( 5.2\)
- Solids content \( 51\) to \( 52\%\)
- Grit level (200 mesh) \( 20\) to \( 35\) mg/kg
E. Persulfate - Metabisulfite Initiated Vinyl Acetate - Vinyl Versatate Copolymer Latex

E.1 Formulation (percent by weight)

1. Initial charge:
   - Water 41.975%
   - CELLOSIZE EP 300 1.0%
   - Nonylphenol (20) ethoxylate (80% aqueous solution) 0.61%
   - Sodium dodecylbenzene sulfonate (10% aqueous solution) 2.8%
   - Antifoam 0.04%
   - Sodium bicarbonate 0.075%

2. Initial system:
   - Initiator 1:
     - Water 1.72%
     - Ammonium persulfate 0.18%
   - Initiator 2:
     - Water 1.72%
     - Sodium metabisulfite 0.18%

3. Monomer mixture:
   - Vinyl acetate 34.6%
   - Vinyl versatate 15.0%

E.2 Procedure

1. Charge the reactor with the initial charge and 8% of monomer mixture.
2. Heat the reactor content to 60°C.
3. Add 25% of initiator 1 and 25% of initiator 2 over 10 minutes at 60°C.
4. While holding the reactor at 60°C, charge the remaining monomer mixture and initiators 1 and 2 over a period of 3 hours.
5. After the addition of the monomer mixture and initiators is complete, hold for one hour at 60°C (cook-out period).
6. Cool to ambient temperature and discharge reactor.

E.3 Latex properties

- Brookfield RVT viscosity (50 rpm, spindle 5, 20°C) 1600 to 2100 mPa•s
- pH 4.7 to 4.8
- Solids content 50 to 51%
- Grit level (200 mesh) 30 to 250 mg/kg
F. Vinyl Acetate - Vinyl Versatate Latex Binder For Premium Quality Paints

F.1 Formulation (percent by weight)

1. Initial charge:
   - Water, demineralized 31.026%
   - RHODACAL™ DS10 (10% aqueous solution) 1.55%
   - Potassium persulfate 0.052%
   - Borax 0.26%
   - Acetic acid 0.103%
   - CELLSIZE QP 300 1.03%

2. Monomer pre-emulsion:
   - Water, demineralized 6.93%
   - DESHCOFIX™ 202 1.03%
   - Vinyl acetate 36.19%
   - Vinyl versatate 15.51%

3. Initiator solution:
   - Water, demineralized 6.20%
   - Potassium persulfate 0.119%

F.2 Procedure

1. Heat the initial reactor charge to 60-65°C while flushing the reactor with nitrogen.
2. Add 5% of the monomer pre-emulsion to the reactor and heat to 76°C.
3. Add the remaining monomer pre-emulsion during a period of 3 hours. In the meantime, add the initiator solution into the reactor by a separate stream for a period of 3 hours and 15 minutes.
4. At the end of the initiator solution addition period, heat the latex to 80°C. Maintain this temperature for an additional period of 2 hours.

F.3 Latex properties

- Brookfield RTV viscosity 2100 mPa•s
- pH 4.4
- Solids content 53.5%

The latex is suitable for the manufacture of high quality interior and exterior emulsion paint types. Optionally the vinyl versatate/vinyl acetate ratio is changed from 70/30 to 75/25 for economy exterior paints, or 80/20 for economy interior paint types. This can be done without further changes in the latex formulation, but the hydrolytic stability of the latex will be slightly lower.

The latex shows an excellent overall stability, as can be expected from colloid-stabilized vinyl versatate latex types. The formulation contains a nonionic surfactant which is NPE-free.

This latex is also characterized by a good water absorption resistance.

† This formulation has been developed by Resolution Performance Products, previously Shell Chemicals Europe, which has given us the permission to include it in our literature.
G. Vinyl Acetate - Butyl Acrylate Latex

G1. Formulation (percent by weight)

1. Initial charge:
   - Deionized water 40.0%
   - Sodium acetate 0.13%
   - Nonylphenol (50) ethoxylate 1.6%
   - Sodium lauryl sulfate 0.27%
   - Ethylene glycol 0.5%
   - CELLOSE EP 09 1.0%

2. Monomer charge:
   - Vinyl acetate 43.3%
   - Butyl acrylate 10.0%

3. Initiator system:
   - Ammonium persulfate 0.1%
   - Deionized water 3.1%

G2. Procedure

1. Charge the reactor with the initial charge, add 10% of the monomer charge and adjust the temperature to 70°C, allowing the monomer to be emulsified for 10 minutes.
2. Add 15% of the initiator and heat the reactor to a temperature of 75°C, prepolymerization for 10 minutes.
3. The remainder of the monomer charge is added over a period of 3 hours together with 80% of the initiator.
4. Postpolymerization for 30 minutes with the remaining 5% initiator solution.

G3. Latex properties

- Brookfield RVT viscosity (50 rpm, spindle 4, 20°C): 1000 to 2000 mPa·s
- pH: 4.6
- Solids content: 55%
- Grit level (200 mesh): 20 to 30 mg/kg
H. All-Acrylic Latex

H.1 Formulation (percent by weight)

1. Initial charge:
   - Deionized water 16.53%
   - Triethanolamine 0.4%

2. Monomer pre-emulsion:
   - Deionized water 16.8%
   - LUTESOL™ A030 2.07%
   - EMULPHOR™ OPS 2.07%
   - Butyl acrylate 23.1%
   - Methyl methacrylate 22.4%
   - Methacrylic acid 0.7%

3. Initiator 1:
   - Ammonium persulfate 0.11%
   - Deionized water 2.82%

4. Initiator 2:
   - Sodium formaldehyde sulfoxylate 0.045%
   - Deionized water 2.815%

5. Protective colloid charge:
   - CELLOSIZE EP 09 0.14%
   - Deionized water 10.0%

H.2 Procedure

1. Prepare pre-emulsion first: dissolve the surfactants in water and then add the monomers under high shear.
2. Place the initial charge in the reactor and heat to 65°C under nitrogen.
3. Feed pre-emulsion and initiators into the reactor over a period of 3 hours at 65°C.
4. After 2 hours of addition, feed the CELLOSIZE HEC solution during the remaining 1 hour.
5. After all reactants are charged, hold at 65°C for 30 minutes (postpolymerization cook-out).
6. After cooling to room temperature, adjust the pH to 8.0 with ammonium hydroxide.

H.3 Latex properties

- Brookfield LVT viscosity (60 rpm, spindle 3, 20°C): 1000 to 2000 mPa•s
- pH: 8.0
- Solids content: 50%
- Grit level (200 mesh): 10 to 40 mg/kg
References


Glossary

BINDER: See latex.
BOUND WATER: The water layer around a latex particle which is bound onto the surface of the particle by the hydrophilic molecules (e.g., HEC) present on that surface. This “bound” water stands in dynamic equilibrium with the “free” water of the continuous phase.
CHAIN TRANSFER AGENT: A chemical capable of reaction with a radical (growing polymer, HEC radical) which results in a termination of the existing radical. The chain transfer agent becomes thereby a radical which can induce further polymerization on a new site.
COAGULATION: Phenomenon where the latex system becomes a solid mass.
COAGULUM: See grit.
COLLOID: Polymeric substance swellable or soluble in water.
DEGREE OF POLYMERIZATION: The number of monomers per polymer molecule. There is normally a distribution of the degree of polymerization which is characterized by an average degree of polymerization.
DEGREE OF SUBSTITUTION: Average number of hydroxyl positions on each anhydroglucose unit that have been substituted. Abbreviation: DS. Maximum value: 3.
EMULSION: System composed of two liquids, not soluble in each other, where one acts as a continuous phase in which droplets of the second component are dispersed. For instance, monomers dispersed in an aqueous system stabilized by surfactants.
EMULSION POLYMERIZATION: A process in which an emulsion of water-insoluble monomers in water is converted to a dispersion of polymer particles in water (see latex) under the influence of a water soluble initiator system.
GRAFTING: The process whereby the hydroxyethyl cellulose becomes chemically attached onto the latex particle.
GRIT: Large polymer particles formed during or after polymerization which have to be removed by filtration or otherwise can create application problems.

HYDRATION TIME: The time after which CELLOSIZE HEC starts to build viscosity after being introduced into water. This time depends on temperature, water quality (including pH) and the type of CELLOSIZE HEC.

INITIATOR: A chemical or a chemical system which, under certain temperature conditions, produces radicals which initiate the polymerization reaction. Initiators are classified as either thermal initiators [chemicals such as ammonium persulfate which decompose at elevated temperatures (+80°C) to generate radicals] or redox initiators [chemical systems such as persulfate/bisulfite reacting under modest temperatures (40-60°C) to generate radicals].

LATEX: An aqueous dispersion of stabilized polymer particles.

MICELLE: Agglomeration of surfactant molecules in aqueous media. The hydrophobic moieties of the surfactant molecules are oriented to the inside of the micelle and the hydrophilic part is oriented outward to the aqueous phase.

MOLAR SUBSTITUTION: Average number of ethylene oxide molecules that have reacted with each anhydroglucose unit. Abbreviation: MS.

MONOMER: A molecule capable of undergoing polymerization. It is typically characterized by an activated carbon-carbon unsaturated bond. Examples include vinyl acetate, vinyl versatate, 2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate, styrene, etc.

PROTECTIVE COLLOID: A colloid like HEC capable of stabilizing a latex by steric stabilization due to its presence at the surface of the polymer particles.

POLYMER: A substance which consists of polymeric molecules. These molecules are composed of a repetition of one or a few building blocks. These building blocks or monomers are converted during the polymerization process to chain formed polymers. If only one building block is used to produce the polymer, then the polymer is called a homopolymer. If two or more building blocks are used to produce the polymer, then the polymer is called a copolymer.

RADICAL: A chemical entity characterized by an atom bearing a lone electron which makes this chemical entity reactive. Radicals are produced by the initiator and these radicals react with the monomer to produce monomer radicals which propagate with other monomers to form a polymeric molecule.

SURFACTANT: Chemical compound which contains in the same molecule a hydrophilic (water-liking) and a hydrophobic (water-hating) group.

SYNERESIS: Phenomenon whereby during storage of a latex an aqueous layer is formed on top of the formulation. The latex can be homogenized easily by stirring.
For more information, complete literature, and product samples, you can reach a Dow representative at the following numbers:

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