

Latex Hydraulic Cement Additives

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This paper describes latexes used to modify hydraulic cement mixes. It includes definitions and brief descriptions of the history, chemistry, types, and production of latexes, together with an explanation of how latex modifies hydraulic cement, and discusses the problems and advantages associated with such systems.

What is a latex?

As reported in the literature (1), an accepted definition is a dispersion of organic polymer particles in water.

But this really doesn't tell you very much. What does it look like? What is an organic polymer? Most latexes or latices are milky fluids that are generally white to off-white in color. Their consistency can vary from very fluid to very viscous.

What is meant by an organic polymer?

This can be defined as a substance that is composed of giant molecules and that has been formed by the union of a considerable number of simple molecules, usually many tens of thousands.

The simple molecules are known as monomers and the reaction that combines them is called polymerization. The polymer may be a homopolymer if it is made by the polymerization of one monomer, or a copolymer when two or more monomers are polymerized.

The first reference to latex was in the early 16th century when the Spanish explorers reported that the South American Indians were making rubber footwear by standing in latex that was obtained from trees. That tree, known as *Hevea brasiliensis*, produces latex naturally, which, of course, is known as natural rubber latex (NRL).

Seedlings of those trees were transferred from South America to Europe; and from Europe, a few were taken to Malaya in the Far East. From those few seedlings, huge plantations and a large industry have grown. The latex, obtained from the tree by a process known as tapping, may be concentrated to be sold as latex or coagulated and dried to be sold as rubber. Production of natural rubber latex in Malaya for 1984 exceeded 200,000 metric tons.

Natural rubber latex is a dispersion of polyisoprene (a homopolymer) that is polymerized and formed into a latex by the tree. Incidentally, NRL has been, and in some places continues to be, used in conjunction with hydraulic cements. In 1924, a patent was granted to Lefebure for the combined use of NRL and cement (2).

Until early in the 20th century, the only available latex was natural rubber latex; then synthetic latexes started to appear on the scene.

Since World War II, there has been a tremendous increase

in the number and type of synthetic polymer latexes that have been made and are commercially available.

The following is a list of the majority of latex types used with hydraulic cements today:

- Styrene-butadiene copolymers (S-B)
- Polyacrylic esters (PAE)
- Styrene-acrylic copolymers (S-A)
- Vinyl acetate homopolymers (PVA)
- Vinyl acetate-ethylene copolymers (VAE)
- Vinyl acetate-acrylic copolymers (VAC)
- Vinyl acetate-vinyl ester of versatic acid copolymers (VA-VEOVA)

This list is not all inclusive. Many other types of latexes are made, probably have been tested, and possibly are being used with hydraulic cements. Some of the latexes listed above are used with hydraulic cements other than portland; and in some cases, the mixes do not contain any aggregate. For this reason, they are referred to as additives rather than the more usual term, admixtures.

All of the latexes listed above are manufactured by a process known as emulsion polymerization and therefore are sometimes referred to as emulsions.

The basic process involves mixing the monomer(s) with water, a stabilizer, and an initiator. The initiator generates a free radical that causes the monomer(s) to polymerize by chain addition.

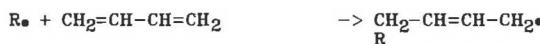
An example of chain addition polymerization is given in Figure 1. The free radical reacts with a molecule of butadiene (or styrene), and the resultant molecule further reacts with a molecule of styrene (or butadiene). This chain of molecules continues to grow until the free radical either no longer contacts a suitable molecule or contacts a chemical that "absorbs" it.

A typical recipe for emulsion polymerization is given in Figure 2. The usual method of polymerization is to charge the water, the stabilizers, the other ingredients, and part of the monomer(s) to the reactor under agitation. The temperature is increased to a desired point, then the initiator system is fed to the reactor followed by the remainder of the monomer(s). By temperature control and possibly other chemical additions, the reaction is normally taken to a 90 to 99 percent conversion. Excess monomer(s) are reduced to acceptable levels by a process known as stripping.

The resultant latex may be concentrated or diluted, and small levels of materials such as preservatives and stabilizers may be added. Many other ingredients are used in polymerization; they are incorporated for a myriad of reasons, such as controlling pH, particle size, and molecular weight.

Many, many latexes are on the market, but about 95 percent of them are not suitable for use with hydraulic cements.

1. Free Radical & Butadiene



2. Copolymerization with Styrene

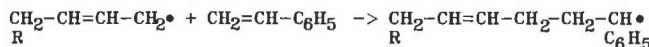


FIGURE 1 Free radical polymerization of butadiene and styrene (*I*).

Latexes can be divided into three classes according to the type of electrical charge on the particle, which is determined by the type of stabilizers: cationic (positively charged), anionic (negatively charged), and nonionic (no charge). In general, cationic or anionic latexes are not suitable for use with hydraulic cements because they lack the necessary stability. Most latexes used with portland cement are stabilized primarily with nonionic stabilizers. Typical recipes for some of the latexes used with portland cement are given in Figures 3, 4, and 5.

The preservatives added to the latex after polymerization usually provide protection against bacteria contamination and give improved aging resistance. Sometimes additional stabilizers are added to provide more stability. Also, defoam or antifoam agents may be added to reduce air entrainment when the latex is mixed with the cement and aggregates.

PRINCIPLE OF LATEX MODIFICATION

Classical theories on the principle of latex modification of hydraulic cement concrete and mortars have appeared in the literature (3, 4). Latex modification is governed by two processes: cement hydration and latex film formation. Generally the cement hydration process precedes the film formation (5), except at surfaces where loss of water by evaporation causes the latex film to form faster than the cement hydrates. It is believed that a co-matrix phase, which consists of the cement gel and latex polymer, is formed as the binder for the mix.

The process of forming the polymer film from the latex is usually referred to as coalescence.

When latex is mixed with fresh cement mortar or concrete, the organic polymer particles are uniformly dispersed in the cement paste. In such latex-cement paste, the cement gel is gradually formed by cement hydration. With water loss due to the development of the cement gel structure and to evaporation, the polymer particles of the latex are gradually confined in the capillary pores.

As cement hydration and evaporation loss continue, the capillary water is reduced and the polymer particles flocculate

	Parts by Weight
Monomers	100.0
Stabilizer	1.0 — 10.0
Initiator	0.1 — 2.0
Water	80.0 — 150.0
Other Ingredients	0.0 — 10.0

FIGURE 2 Typical recipe for emulsion polymerization (*I*).

	Parts by Weight
Vinyl acetate	100.0
Partially hydrolyzed polyvinyl alcohol	6.0
Sodium bicarbonate	0.3
Hydrogen peroxide 35%	0.7
Sodium formaldehyde sulfoxylate	0.5
Water	80.0

FIGURE 3 Vinyl acetate homopolymer latex (*I*).

to form a continuous close-packed layer on the surfaces of the cement gel-unhydrated cement particle mixtures. These layers simultaneously adhere to the mixtures and the silicate layer of the aggregate surfaces. One should bear in mind that the size of the pores in the cement paste ranges from a few angstroms to several thousand angstroms; whereas the particle size of latexes typically used with cement ranges from 500 to 5,000 angstroms (6). Ultimately, with water loss by cement hydration and evaporation, the close-packed polymer particles on the cement hydrates coalesce into continuous films or membranes.

These films or membranes bind the cement hydrates together, resulting in a monolithic network in which polymer films interpenetrate the cement-hydrate phase. Such a structure acts as the co-matrix phase for latex-modified mortar and concrete, with the aggregates being bound by such a matrix.

It is generally considered that unmodified hardened cement paste is predominantly an agglomerated structure of calcium silicate hydrates and calcium hydroxide bound together by relatively weak van der Waal's forces. Consequently, microcracks occur easily in such a paste under stress, leading to the low tensile strength and fracture toughness of ordinary cement mortar and concrete.

By contrast, in latex-modified mortar and concrete, it appears that the microcracks are bridged by the polymer films or membranes which greatly reduce crack propagation and simultaneously give a strong cement hydrate-aggregate bond. This effect increases with increasing latex content and leads to increased tensile strength and fracture toughness.

The sealing effect due to the films or membranes formed in the structure also provide a considerable increase in water-

	Parts by Weight
Ethyl acrylate	98.0
A vinyl carboxylic acid	2.0
Nonionic surfactant	6.0*
Anionic surfactant	0.3**
Sodium formaldehyde sulfoxylate	0.1
Caustic soda	0.2
Peroxide	0.1
Water	100.0

*The nonionic surfactants may be nonyl phenols reacted with 20–40 molecules of ethylene oxide.

**The low levels of anionic surfactant are used to control the rate of polymerization.

FIGURE 4 Polyacrylic latex (*I*).

Parts by Weight		
Styrene	64.0	
Butadiene	35.0	
A vinyl carboxylic acid	1.0	
Nonionic surfactant	7.0*	
Anionic surfactant	0.1**	
Ammonium persulfate	0.2	
Water	105.0	

*The nonionic surfactants may be nonyl phenols reacted with 20-40 molecules of ethylene oxide.

**The low levels of anionic surfactant are used to control the rate of polymerization.

FIGURE 5 Styrene-butadiene copolymer latex (I).

proofness or watertightness, resistance to moisture transmission, resistance to vapor penetration, chemical resistance, and freeze-thaw resistance. Such effects are promoted with increasing latex content. Excess latex and/or air entrainment causes discontinuities in the formed monolithic network structure, resulting in a reduction of such characteristics. In most latex-modified portland cement aggregate mixtures, the optimum level is between 10 and 20 percent of dry polymer on the cement (7).

Some latexes used with hydraulic cement mixes contain reactive groups. It is probable that some chemical reactions may take place between these groups and metallic ions and salts in the surfaces of the cement gel and the aggregates. Such reactions are expected to improve the bond between the cement hydrates and aggregates with subsequent improvements in the properties of the hardened latex-modified mortars and concretes.

Wagner studied the influence of latex modification on the rate of specific area development of latex-modified pastes (5). According to his results, the initial rate of cement hydration can be accelerated or retarded by the addition of the latexes, depending on their chemical nature. However, the specific surface area of all the pastes after a 28-day cure is comparable, indicating that while latex modification may have some effect on the initial hydration process, it has little effect on the final hydration of the cement.

According to Ohama and Shiroishida (8) or Kasia et al. (9), the porosity or pore volume of the latex-modified mortars differs from unmodified mortar in that the former has a lower number of pores in the larger radius of 0.2 microns or more, but significantly more in the smaller radius of 750 angstroms or less. Also the total porosity or pore volume tends to decrease with increasing polymer-cement ratios. This can be found to contribute to improvements in the impermeability to liquids, resistance to carbonation, and freeze-thaw durability.

PROBLEMS WITH LATEX-MODIFIED CONCRETES AND MORTARS

Which Latex?

One of the major problems associated with latex-modified concretes and mortars is that most users do not have an adequate understanding of latex. A latex is a latex, right? WRONG!

Each type of polymer latex can and usually does impart different properties to hydraulic cement mixtures. Also, it must be realized that within each type of latex, particularly copolymers, there can be many variations which can and do give different properties. If there is a doubt, the latex supplier should be contacted. There have been jobs where the wrong latex was used, resulting in disastrous consequences. For example, a vinyl acetate homopolymer was used in mortar to hold air conditioning units in the walls of a high-rise apartment. The moisture condensation caused by the air conditioners was sufficient, with the high pH of the portland cement mortar, to hydrolyze the homopolymer, causing the air conditioners to fall out.

Cost

Using latex in hydraulic cement mixes generally increases the cost of raw materials by at least a factor of two. A comparison of an unmodified and an S-B latex-modified portland cement concretes is given in Figure 6.

Mud-Cracking

If a latex-modified mix is being placed when the ambient conditions are such that the surface of the mix is exposed to

UNMODIFIED CONCRETE

Ingredient	Weight lb/yd ³	cost \$/lb	Extension \$/yd ³
Portland Cement, Type I	658	0.0580	38.16
Concrete Sand	1645	0.0048	90
Pea Gravel	1315	0.0078	10.27

Cost per cubic yard = \$ 56.33

LATEX-MODIFIED CONCRETE

Ingredient	Weight lb/yd ³	cost \$/lb	Extension \$/yd ³
Portland Cement, Type I	658	0.0580	38.16
Concrete Sand	1645	0.0048	7.90
Pea Gravel	1315	0.0078	10.27
Styrene-butadiene latex	207	0.4850	100.40

Cost per cubic yard = \$ 156.73

FIGURE 6 Cost comparison of UMC and LMC.

good drying conditions, i.e., windy and low humidity, the polymer particles of the latex may coalesce to form a latex skin on the surface of the mix prior to noticeable cement hydration.

When this occurs, the skin or crust may exhibit mud-cracking due to shrinkage of the latex skin before the cement hydration has proceeded enough so that the mix has sufficient strength to withstand the shrinkage forces. Consequently steps must be taken to avoid such an occurrence. With S-B latex-modified concretes used for bridge-deck overlays, these steps usually involve covering the concrete as soon as possible with wet burlap and plastic sheeting. This process usually costs time and money and, if performed incorrectly, can give the job a very poor appearance.

Mixing Times

All latexes used with hydraulic cements contain relatively high levels of stabilizers or "soaps." As in a washing machine, these soaps, if mixed sufficiently, will incorporate air and form a froth. In hydraulic cement mixes, this process can result in unacceptably high air contents, which, as illustrated in Figure 7 with a PAE-latex-modified mortar, reduces strength properties. Consequently, when latex-modified hydraulic cement concrete or mortar is being prepared, it is essential that the mixing time is kept to a minimum, usually less than 3 min. This requirement eliminates the use of normal ready-mix trucks; and for large jobs, demands the use of the more expensive mobile-mixer.

SO WHY USE LATEX?

As mentioned when explaining how latex modifies hydraulic cement concretes or mortars, the latex and the cement form a co-matrix to bind the aggregates. This co-matrix is superior to unmodified mixes in bridging the microcracks, resulting in increased resistance to movement of fluids within the concrete and in increased strength properties. As the latex-cement co-matrix improves adhesion to the aggregates in the mix, it also improves adhesion of the mix to most substrates. In fact, when placing latex-modified concrete or mortar (LMC), one should always clean the tools before the mix hardens or they become very difficult to clean.

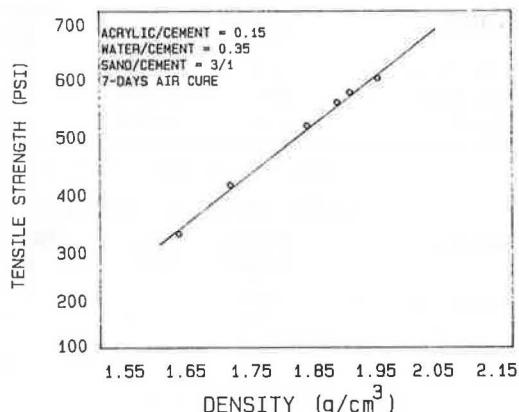


FIGURE 7 Tensile strength vs. density (16).

	UMC	SB-LMC
FHWA 90 ponding test (10)		
0.75 inch depth, 1b chloride	10.53	1.37 (10)
0.75 inch depth, 1b chloride	7.70	1.08 (11)
ASTM T277-831, Rapid Determination (12)		
Coulombs	2560	876

FIGURE 8 Resistance to penetration of chlorides

The only two economical reasons for using latex modification are to increase adhesion or to improve resistance to movement of fluids through the hardened cement mix. Improvements in some strength properties are also obtained, but there are usually cheaper ways to obtain similar improvements if this is all that is required. Incorporation of latex does not improve compressive strength; in fact, usually a decrease is observed.

Resistance to Penetration of Fluids

Resistance to movement of fluids through the concrete provides protection to the concrete. Work by the Federal Highway Administration (10), the Department of Transportation of Louisiana (11), and the Portland Cement Association (12) showed improvements in freeze-thaw and scaling resistance and improvements in resistance to penetration of water-soluble salts of S-B latex-modified concretes in comparison with similar unmodified mixes (Figures 8 and 9).

Figure 10 illustrates improvement in resistance to penetration of gases, such as carbon dioxide, with both S-B and VAE latex-modified mortars, confirming work by Ohama (13). In this work, concrete or mortar cylinders are exposed to a vacuum and then to carbon dioxide gas under pressure for specific time periods. The cylinders are then split using a splitting tensile device. Immediately, the split surface is painted with a colorless aqueous solution of phenolphthalein. The latter, a pH indicator, indicates where the carbon dioxide gas has not penetrated by changing to a red-purple color.

Improvement in Adhesion

Improvements in adhesion of latex-modified cement mixes over similar unmodified mixes have been shown with different

	UMC	SB-LMC
1. FREEZE-THAW - ASTM C-666 (B)		
Durability factor	14	78
2. SCALING RESISTANCE - ASTM 672		
Cycles	14	52
Durability factor	5	1

FIGURE 9 Resistance to freeze-thaw and scaling (11).

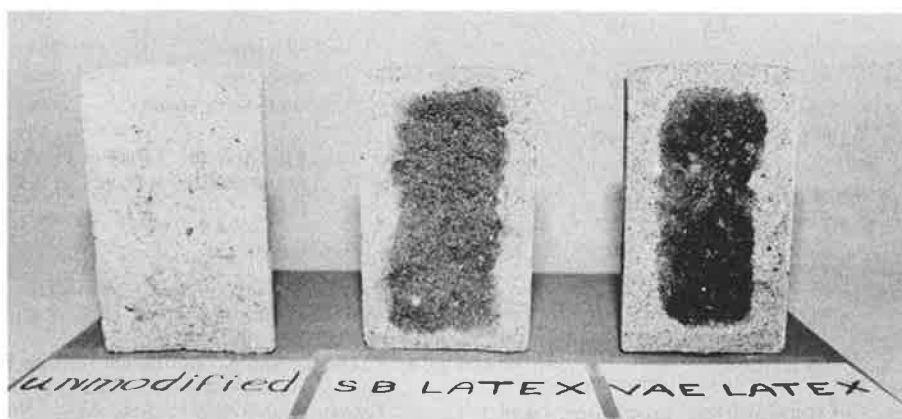


FIGURE 10 Comparison of UMC and LMC for carbonation resistance.

latexes (14-16) and are illustrated in Figures 11 and 12 with S-B and PAE latex-modified mixes.

Improvements in Strength

Figure 13 shows that flexural strengths and splitting tensile values of S-B latex-modified concrete are significantly higher than for similar unmodified mixes (11). Improvements in abrasion resistance caused by latex modification of cement mixes has been shown by both Ohama (17) and Alexanderson (18). The latter's work, with styrene-butadiene latex-modified mixes, is shown in Figure 14. It should be noted that measurably lower values of these strength properties are obtained if the latex-modified concrete or mortar is tested in the wet state.

A Forgiving System

Although latex-modified mixes have some unique characteristics that require special handling when being placed, basi-

cally the same techniques and practices are used as with unmodified cement mixes. Also, LMC is a very forgiving system. Because the latex-cement co-matrix significantly reduces the movement of fluids through the concrete, a latex-modified mix does not require curing compounds, fog sprays, or water soaking to ensure adequate water for hydration and strength development of the cement. Once it is strong enough to withstand early shrinkage forces, usually 24 hr or less, the concrete will retain sufficient water to ensure adequate hydration of the cement. Comparison of strength attributes of unmodified and PAE latex-modified mortars, cured wet and dry respectively, confirms this postulation (16).

Although latex-modified concretes and mortars can have high air contents, work by Kuhlmann and Foor (19) has shown that high air contents have little effect on permeability of S-B latex-modified mixes, as measured by the rapid method AASHTO T277-83I. Figure 15, which gives confirmation, shows data obtained from an S-B LMC overlay in a parking garage in Madison, Wisconsin, placed in June 1986. The permeabilities were determined on cores taken in May 1987.

Figure 16, which shows data obtained by Kuhlmann (15), illustrates that the mud-cracking tendencies of S-B LMC have no apparent effect on permeability resistance.

CURE days	UMC psi	SB-LMC psi
3	161	262
7	181	278
14	215	327
28	243	334
90	256	365

FIGURE 11 Tension bond (15).

PAE-CEMENT Ratio	Cure	Shear Bond psi	Adhesion Mode
0.00	dry	45	Adhesive
0.00	wet	185	Adhesive
0.10	dry	500	Cohesive
0.15	dry	650	Cohesive
0.20	dry	550	Cohesive

FIGURE 12 Shear bond adhesion (16).

	UMC	SB -LMC
Flexural Strength, ASTM C 78,psi	441	538
Splitting Tensile, ASTM C 496,psi	639	1061

FIGURE 13 Strength properties (11).

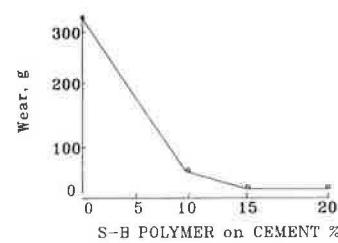


FIGURE 14 Abrasion resistance (18).

	A	B
Air content, %	7.3	>10.0
Compressive strength 28 days, psi	5360	3520
Permeability resistance, 11 months, coulombs	515	415

FIGURE 15 Effect of air content on permeability resistance of S-B LMC.

SUMMARY

In summary, the use of latex with hydraulic cements results in a co-matrix that gives improvements in adhesion, resistance to transmission of fluids, and some strength properties. Generally this use is justified economically only to improve adhesion and/or water resistance of the system. The type of latex must be carefully selected to ensure its suitability for use with hydraulic cements and for the intended application. Although latex-modified mixes require short mixing times and often require steps to avoid mud-cracking, the system uses normal hydraulic cement techniques except that normal curing is not required.

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	Permeability Resistance coulombs
No cracks	260
Mud-cracks	260
Half-depth cracks	700

FIGURE 16 Effect of cracking on permeability resistance of S-B LMC (15).