EASTMAN

Success with **water-dispersible sulfopolyesters**

High performance polymers for formulated products

Thermoplastic, aromatic polyesters are high performance polymers widely used in textiles and packaging applications because of their strength, toughness, optical clarity, safety profile, recyclability, and ease of processing. Eastman is a global leader in specialty copolyesters used in packaging and consumer products. In the 1970s, Eastman researchers invented water-dispersible sulfopolyesters to translate the benefits of polyesters into waterborne formulated products. Eastman water-dispersible sulfopolyesters are amorphous, aromatic polymers containing anionic sulfonate groups. Eastman's portfolio of sulfopolyesters spans a broad range of physical properties to satisfy performance requirements in coatings, inks, adhesives, textile sizing, and personal care applications.

Benefits

- Disperses readily
- Low-viscosity dispersions—good for gravure and spray applications
- Dispersion/emulsification capacity for oils, waxes, silicones, and pigments—improves formulation stability
- High gloss—smooth, dense films with high refractive index
- Excellent film formation
- Low tack—for high-T_g polymers
- Water/humidity-resistant films—for low-charge-density polymers
- Fast drying—higher running speeds for printing and roll-coating operations
- Low odor—no need for amines
- Stable pH and viscosity
- Low foaming—no surfactant
- Stable with metallic pigments
- Near neutral pH
- Excellent adhesion to various substrates—wood, aluminum, fibers, skin, and hair

Product line

Eastman water-dispersible sulfopolyesters are available in a variety of solid and liquid product forms, with a range of physical properties that enable their use in diverse applications. Several sulfopolyesters are available in both solid and dispersion form.

Sulfopolyester composition and properties

Composition

Sulfopolyesters are prepared by melt-phase polymerization of glycols and aromatic diacids. Typical monomers used to produce water-dispersible sulfopolyesters are isophthalic acid (IPA), 5-sodiosulfoisophthalic acid (5-SSIPA), 1,4-cyclohexanedimethanol (CHDM), and diethylene glycol (DEG).

Eastman AQ™ 38S and 55S polymers and Eastman AQ™ 48 ultra polymer contain these four monomers but in different ratios. For cosmetics and personal care applications, they have been assigned the same INCI (International Nomenclature of Cosmetic Ingredients) name, Polyester-5.

Because water-dispersible sulfopolyesters are produced under conditions of excess diol, the polymer chains are mostly terminated by hydroxyl groups. Most have hydroxyl and carboxyl numbers of ~10 and ~2, respectively.

Molecular weight

Eastman water-dispersible sulfopolyesters typically have number-average molecular weight M_n = 5–15 kDa, weight-average molecular weight M_w = 20–30 kDa, and polydispersity index $M_w/M_n \sim 2$.

Glass transition temperature

Eastman sulfopolyesters span a range of glass transition temperatures (T_g) from ~0° to ~65°C. See Table 1.

Figure 1. Polyester-5

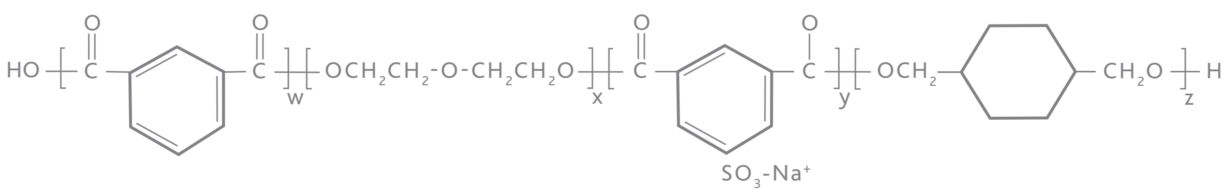


Table 1. Typical properties of Eastman water-dispersible sulfopolyesters

Approximate T_g[a] (°C)	Calculated charge density (meq/g)	Solid form	Dispersion form[b]
0	0.32	Eastman AQ™ 1350 copolyester	—
3	0.38	Eastman AQ 1950 copolyester	—
10	0.38	Eastman AQ 2350 copolyester	—
29	0.45	—	Eastek™ 1400 polymer dispersion
35	0.47	—	Eastek 1300 polymer dispersion
38	0.43	Eastman AQ 38S polymer	Eastek 1000 polymer dispersion
48	0.89	Eastman AQ 48 ultra polymer	—
55	0.66	Eastman AQ 55S polymer	Eastek 1100 polymer dispersion
63	0.33	Eastman AQ 65S polymer	Eastek 1200 polymer dispersion

[a]Properties reported here are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the values given.
[b]Eastek products are supplied as 30% solids in aqueous dispersions. The exceptions are Eastek 1100 which contains 33% solids and Eastek 1200 which contains 2% n-propanol.

Charge density

Cationic and anionic polymers are characterized by their charge density, usually expressed as milliequivalents (meq) of anionic or cationic groups per gram of polymer. Calculated charge densities of Eastman water-dispersible sulfopolyesters range from 0.3 to 0.9 meq/g. See Table 1. Sulfopolyesters with high charge density are more easily dispersed in water, form smaller aggregates in dispersions, and are preferred as dispersants. Sulfopolyesters with low charge density produce films with better water/humidity resistance.

Refractive index

Compared to many commonly used formulation polymers, aromatic sulfopolyesters have high refractive index, from ~1.55 to ~1.57.

Sulfopolyesters disperse in water

An important distinction between sulfopolyesters and water-soluble polymers (e.g., polyvinyl alcohol or polyvinyl pyrrolidone) is that dispersed sulfopolyesters spontaneously form small negatively charged aggregates suspended in water. These aggregates are prevented from precipitation by electrostatic repulsion. The size of dispersed sulfopolyester aggregates, measured by light scattering and chromatographic particle size analysis, ranges from 10 to 30 nm diameter and depends inversely on charge density. Sulfopolyester aggregates in this size range have aggregation numbers of 10–100 polymer chains per particle. Consequently, the aggregates resemble surfactant micelles and are much smaller than the particles in typical emulsion polymer latexes.

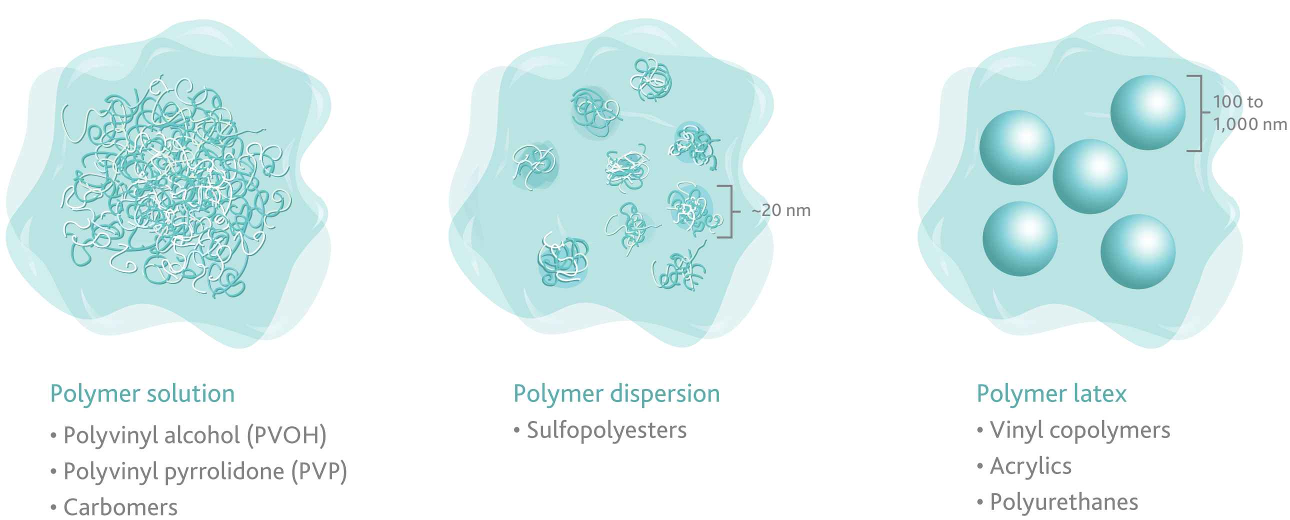
Preparation of dispersions

Sulfopolyesters with charge density >0.35 meq/g disperse readily in water at modest temperatures (40°–80°C) without the assistance of emulsifiers, organic cosolvents, inorganic bases, amines, or other additives. Complete dispersion is normally achieved in 20–30 minutes, depending on the sulfopolyester composition and water temperature. Deionized or soft water (total hardness less than 20 mg/kg is recommended for sulfopolyester dispersions because multivalent cations (e.g., Ca^{2+}) can retard the dispersion rate. If multivalent cations are present in sufficient concentration, they can produce opaque or unstable dispersions. Sulfopolyesters with charge density <0.35 meq/g generally require higher dispersion temperatures, longer dispersion times, and/or an organic cosolvent (e.g., 1-propanol).

Viscosity of sulfopolyester dispersions

An important consequence of the particulate nature of dispersed sulfopolyesters is the functional dependence of dispersion viscosity on percent solids. Unlike solution polymers whose chains entangle at low concentration, sulfopolyester dispersions have low viscosity (typically <100 cP) up to 30% w/w. Above 30%, the viscosity rises very rapidly with increasing concentration. In this, they resemble latexes but the viscosity increases at significantly lower percent solids.

Figure 2. Dispersed sulfopolyesters



Stability of sulfopolyester dispersions

Aqueous dispersions of sulfopolyesters are potentially susceptible to two forms of instability: (1) flocculation/precipitation caused by cations, especially multivalent cations, and (2) hydrolysis of dispersed sulfopolyester chains. At high concentration, even monovalent cations (Na^+) can cause the viscosity to increase, potentially leading to gel formation. Sulfopolyesters in aqueous dispersions exhibit good chemical stability at pH 5–7.5. In this pH range, there is no significant change in molecular weight after 1-year storage at room temperature. Below pH 5, acid-catalyzed hydrolysis results in a decrease in molecular weight over time, especially at elevated temperatures. Similarly, above pH 7.5, base-catalyzed hydrolysis (saponification) can result in precipitation.

Emulsification/dispersion capacity of sulfopolyesters

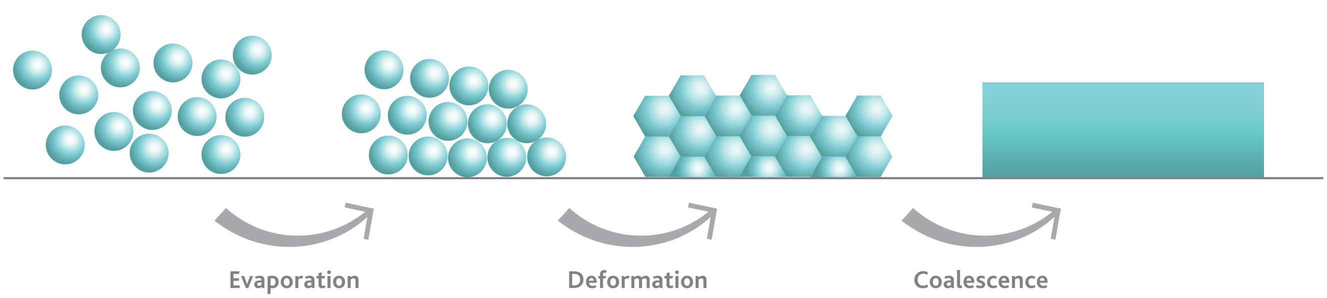
Sulfopolyesters have significant capacity to function as secondary emulsifiers or dispersants for a variety of hydrophobic materials, e.g., vegetable oils, fragrances, waxes, organic UV filters, petrolatum, silicones, and pigments.

- Vegetable oils can be dispersed in aqueous sulfopolyester dispersions up to a weight ratio of 80:1 oil to sulfopolyester.
- Silicone oil (polydimethylsiloxane) emulsions can be produced by high-shear mixing ~70 wt% dimethicone with ~3 wt% Eastman AQ™ 48 ultra polymer in water. Once formed, these emulsions are easily water reducible, indicating the dispersed phase is silicone.
- Waxes can be dispersed in water using sulfopolyesters as polymeric emulsifiers at temperatures above the melting temperature of the waxes. When dispersing waxes, the wax-to-sulfopolyester weight ratio can be as high as 15:1 with up to 45% total solids. Comparison of two sulfopolyesters revealed that the higher-charge-density polymer dispersed the wax faster.
- Dispersed sulfopolyesters also help disperse solid pigments, both organic and inorganic, in water. This performance has been utilized in inks, coatings, and color cosmetics. In cosmetic emulsions, this means that pigments can be added and dispersed in the aqueous phase instead of the oil phase if desired. Pigments can be surface treated with sulfopolyesters to provide water dispersibility.

Film formation

When applied to solid surfaces, aqueous or hydroalcoholic sulfopolyester dispersions dry quickly, producing smooth glossy films. Formation of films from dispersed sulfopolyesters resembles those formed from waterborne latexes.

Figure 3. Formation of films from dispersed sulfopolyesters



Minimum film formation temperature (MFFT)

For conventional polymer latex, the minimum film formation temperature is approximately equal to the T_g of the polymer. For polymers with T_g above ambient temperature, either the coating must be heated or a coalescing agent, typically an organic coalescent, must be added to reduce the T_g of the polymer. Because water-dispersible sulfopolyesters are plasticized by water, the MFFT for the sulfopolyesters is typically about 20°C below the T_g and occurs without added organic coalescent except for the highest-T_g sulfopolyester.

Drying time

It is likely that both the easy coalescence of sulfopolyester aggregates and the fast drying are due, in part, to the very small size of polymer aggregates in sulfopolyester dispersions. Coalescence is also facilitated by hydroplasticization, that is, plasticization of the polymer film by water.

Physical properties of sulfopolyester films

Tack

Sulfopolyesters with T_g > 38°C produce films with low tack. If tack is desired, select a low-T_g polymer or add a nonvolatile plasticizer.

Flexibility

Thin sulfopolyester films with T_g > 45°C are rigid, with <1% elongation at break. The flexibility of sulfopolyesters is easily modified with a variety of plasticizers, e.g., propylene glycol, glycerin, triethyl citrate (TEC), and 2-butoxyethanol.

Water/humidity resistance of sulfopolyester films

As expected, the intrinsic water resistance of sulfopolyester films is inversely dependent on the polymer's charge density; low-charge-density polymers are more water resistant than high-charge-density polymers. Because sulfopolyesters don't disperse in high ionic strength media, they can provide even greater resistance against body fluids, e.g., sweat. This performance benefit has been exploited in sweat-resistant hairstyling products and sunscreens.

The water resistance of a film containing sulfopolyester is highly dependent on the nature of other additives in the formulation; for example, plasticizers that may have been added to improve the film's flexibility. Hydrophobic plasticizers (e.g., triethyl citrate) preserve or enhance water resistance, while a similar amount of a hydrophilic plasticizer (e.g., glycerin) yields a film which will absorb water vapor and disperse in water more readily.

The Na+ cations in a sulfopolyester film are labile and can be exchanged by contact with an aqueous solution containing free multivalent cations, e.g., Ca^{2+}. These will cross-link the sulfopolyester film, greatly increasing its water resistance.

Gloss

Because of the simple relationship between specular reflectivity and the refractive index difference at a smooth interface, the gloss of a smooth polymer surface is determined by the polymer's refractive index. Sulfopolyester dispersions, having small-sized aggregates, form very smooth, glossy films. If a matte finish is desired, conventional mattifying agents (e.g., clays or silica) have been found to work well in sulfopolyester films/coatings.

Health, safety, environmental, and regulatory information

Eastman conducts product safety reviews to help minimize the potential for adverse effects on health and the environment from use of our products, as well as to ensure that product-specific regulatory requirements are met. Eastman's Product Safety and Health team reviews the raw materials, final composition, and manufacturing process steps for our products to help ensure that they comply with applicable laws and regulations. We are committed to developing products that can be manufactured, transported, used, and disposed of or recycled safely.

Eastman AQ linear sulfopolyesters have been the subject of extensive toxicological testing. End points evaluated include acute (oral, dermal, and inhalation) and subchronic (inhalation) toxicity, mutagenicity potential, dermal (acute and repeat exposure), and ocular irritation, as well as sensitization potential. Much of this data comes from studies that were conducted using Eastman AQ™ 55 polymer as a representative prototype of the class of AQ polymers which share very similar chemical compositions and properties. Results from these studies indicate that Eastman AQ linear polyesters can be used in many different applications with adequate safety margins. A summary of these toxicology results is available on request.

For more information, including safety data sheets, technical data sheets, and regulatory information sheets, visit **Eastman.com**. You can also contact your Eastman sales representative directly.

Applications

Table 2 presents known applications of Eastman water-dispersible sulfopolyesters and is intended to stimulate, not stifle, the creativity of formulators. Any of these polymers may provide benefits in these or other applications. For example, Eastman AQ 38S, 48 ultra, and 55S polymers have been reviewed for certain cosmetics applications. However, it is the responsibility of our customers to determine that their use of our product(s) is safe, lawful, and technically suitable in their intended applications. Because of possible changes in the law and regulations as well as possible changes in our products, we recommend that customers continuing to use these products verify their regulatory status periodically.

Table 2. Applications of Eastman water-dispersible sulfopolyesters

Product name	Coating and primers	Personal care and cosmetics	Hot-melt adhesives	Pigment dispersants	Printing inks and overprints	Textile sizes
Dispersion						
Eastek™ 1000 polymer dispersion	X				X	X
Eastek 1100 polymer dispersion	X			X	X	
Eastek 1200 polymer dispersion	X				X	
Eastek 1300 polymer dispersion	X				X	X
Eastek 1400 polymer dispersion	X				X	X
Solid						
Eastman AQ™ 1350 copolyester		X	X			
Eastman AQ 1950 copolyester			X			
Eastman AQ 2350 copolyester			X			
Eastman AQ 38S polymer	X	X			X	X
Eastman AQ 48 ultra polymer		X		X		
Eastman AQ 55S polymer	X	X		X	X	
Eastman AQ 65S polymer	X				X	

Water-dispersible sulfopolyesters possess a combination of properties and performance benefits that commend their use in numerous applications. Their performance in formulated products will ultimately depend on the entire formulation and use conditions. The key to success is selecting the right polymer for your application and combining it with ingredients that augment, not compromise, its performance. Contact an Eastman representative to help you get started.

EASTMAN

The results of **insight**™

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