HITENOL

Polymerizable Surfactants

INTRODUCTION

In emulsion polymerization, emulsifiers (surfactants) play a role to provide stability to the latex (polymer) particles during the polymerization process. However, they may show negative effects to the product afterward. When the latex is used in coatings, the unbond surfactants may migrate through the film forming aggregates that allows penetration of water. The surfactants may also migrate to the air-film interface affecting gloss or to the film-substrate interface affecting adhesion. These adverse effects are caused from desorption of the surfactant molecules from the surface of the latex particles. A promising approach to reduce these negative effects of surfactants that can move freely is to use polymerizable surfactants. The surfactant molecules that provided stability to the latex particles are chemically bonded to the latex particles during the course of the polymerization process and desorption of surfactant molecules from the latex particles and migration inside of the resulting polymer film may be minimized.

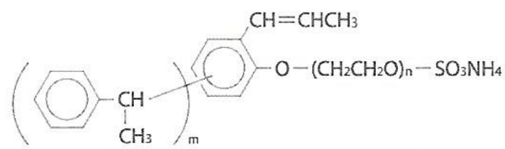
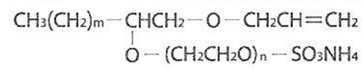
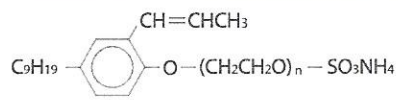
Polymerizable surfactants are designed to chemically bond to the latex polymer particles during polymerization. Films derived from this type of latex are expected to exhibit low degrees of surfactant migration. Therefore the films shall show higher water resistance, improved mechanical stability, compared to films derived from latex polymerized using conventional surfactants.

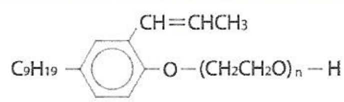
APPLICABLE FIELDS

1. **Emulsifier for Emulsion Polymerization of Synthetic Resins.**
2. **Emulsifier for Emulsion Polymerization of Synthetic Rubber Latexes.**
3. **Dispersant for Suspension Polymerization of Synthetic Resins.**
4. **Various Industrial Emulsifiers and Dispersants.**
5. **Comonomer for Modyfying Resins (Antistatic Agents).**

CHEMICAL STRUCTURE

HITENOL and NOIGEN series are polymerizable surfactants bearing polymerizable groups on their hydrophobic groups. HITENOL AR, KH and BC series are anionic and NOIGEN RN series are nonionic.

Grade	Chemical Structure
HITENOL AR	
HITENOL KH	
HITENOL BC	

Grade	Chemical Structure
NOIGEN RN	

COMPARISON OF HITENOL GRADES

Application	Monomer System	Items Evaluated	HITENOL AR	HITENOL KH	HITENOL BC	Conventional Surfactants
Coating · Adhesive	Acrylic Monomer	Conversion of Surfactants	Excellent	Excellent	Excellent	-
		Low Foaming of Latex	Excellent	Good	Good	Poor
		Water Resistance of Polymer Film	Excellent	Excellent	Excellent	Poor
		Adhesion	Good	Excellent	Good	Fair
Coating	Acrylic-Styrene Monomer	Conversion of Surfactants	Excellent	Fair	Excellent	-
		Low Foaming of Latex	Excellent	Good	Good	Poor
		Water Resistance of Polymer Film	Excellent	Good	Excellent	Poor
Conversion of Surfactants toward Vinyl Acetate			Poor	Excellent	Poor	-

CHEMICAL AND PHYSICAL PROPERTIES

1. ANIONIC SURFACTANTS

Grade		Chemical Description	Appearance	Active Matter	pH (@1%)	HLB
HITENOL	AR-10	Polyoxyethylene styrenated propenyl phenyl ether sulfate ammonium salt	Viscous Liquid, Amber	97.0% minimum	Approx. 7.5	-
	AR-20		Viscous Liquid, Amber	97.0% minimum	Approx. 7.5	-
	AR-1025		Liquid, Yellow	24.0 ~ 26.0%	Approx. 7.5	-
	AR-2020		Liquid, Yellow	19.0 ~ 21.0%	Approx. 7.5	-
HITENOL	KH-05	Polyoxyethylene-1-(allyloxymethyl) alkyl ether sulfate ammonium salt	Viscous Liquid, Yellow	97.0% minimum	Approx. 7.5	-
	KH-10		Viscous Liquid, Yellow	97.0% minimum	Approx. 7.5	-
	KH-1025		Liquid, Yellow	24.0 ~ 26.0%	Approx. 7.5	-
HITENOL	BC-10	Polyoxyethylene nonyl propenyl phenyl ether sulfate ammonium salt	Viscous Liquid, Amber	97.0% minimum	Approx. 7.5	-
	BC-20		Viscous Liquid, Amber	97.0% minimum	Approx. 7.5	-
	BC-1025		Liquid, Yellow	24.0 ~ 26.0%	Approx. 7.5	-
	BC-2020		Liquid, Yellow	19.0 ~ 21.0%	Approx. 7.5	-

1) Wilhelmy method at 25 ℃
2) at 25 ℃

2. NONIONIC SURFACTANTS

Grade		Chemical Description	Appearance	Active Matter	pH (@1%)	HLB
NOIGEN	RN-10	Polyoxyethylene nonyl propenyl phenyl ether	Viscous Liquid, Yellow	99.0% minimum	Approx. 6.0	12.6
	RN-20		Solid, Yellow	99.0% minimum	Approx. 6.0	15.4
	RN-30		Solid, Yellow	99.0% minimum	Approx. 6.0	16.7
	RN-2025		Liquid, Yellow	24.0 ~ 26.0%	Approx. 6.0	15.4
	RN-50		Viscous Liquid, Yellow	64.0 ~ 66.0%	Approx. 6.0	17.9

1) Wilhelmy method at 25 ℃
2) at 25 ℃

Critical Micelle Concentration[1] [mg/l]	Viscosity [mPa·s]				
	20 °C	30 °C	40 °C	50 °C	60 °C
250	182,500	58,000	20,000	6,800	4,000
250	14,700	5,200	2,800	1,600	1,000
250	21[2]		15	-	-
250	13[2]		10	-	-
200	17,500	8,200	2,900	2,100	1,400
200	8,300	3,900	2,200	1,200	800
200	21[2]		15	-	-
100	111,300	44,000	15,800	4,500	2,900
100	13,900	6,800	3,700	1,300	1,000
100	45[2]		35	-	-
100	20[2]		15	-	-

Critical Micelle Concentration[1] [mg/l]	Viscosity [mPa·s]				
	20 °C	30 °C	40 °C	50 °C	60 °C
15	460	270	210	110	50
30	Solid	Solid	470	230	120
60	Solid	Solid	Solid	240	170
30	34[2]		-	-	-
200	4,500	1,900	1,300	690	400

3. SOLUBILITY IN SOLVENTS

Grade		n-Hexane	Isopropyl alcohol	Acetone	Diethyl ether	Methyl ethyl ketone
HITENOL	AR-10	-	±	±	-	±
	AR-20	-	±	±	-	±
HITENOL	KH-05	-	+	+	+	+
	KH-10	-	+	+	+	+
HITENOL	BC-10	-	±	±	±	±
	BC-20	-	±	±	±	±
NOIGEN	RN-10	-	+	+	+	+
	RN-20	-	+	+	+	+
	RN-30	-	+	+	+	+

10% Surfactant concentration at 25 °C

+:Soluble, ±:Slightly Soluble, -:Insoluble

4. SOLUBILITY IN MONOMERS

Grade		Acrylic acid	Butyl acrylate	Ethyl acrylate	2-Ethylhexyl acrylate	Methyl methacrylate	Styrene
HITENOL	AR-10	+	±	±	-	±	+
	AR-20	+	±	±	-	±	+
HITENOL	KH-05	+	+	+	+	+	+
	KH-10	+	+	+	+	+	+
HITENOL	BC-10	+	±	±	±	±	+
	BC-20	+	±	±	±	±	+
NOIGEN	RN-10	+	+	+	+	+	+
	RN-20	+	+	+	+	+	+
	RN-30	+	+	+	+	+	+

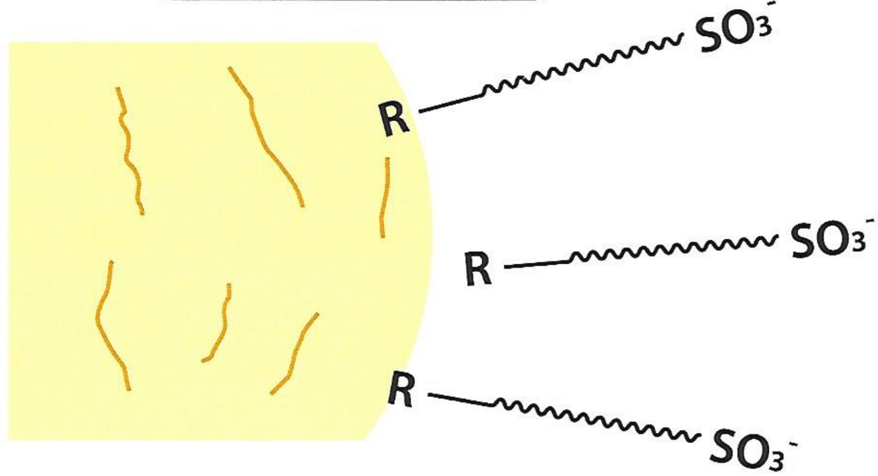
10% Surfactant concentration at 25 °C

+:Soluble, ±:Slightly Soluble, -:Insoluble

QUALITIES AND CHARACTERISTICS

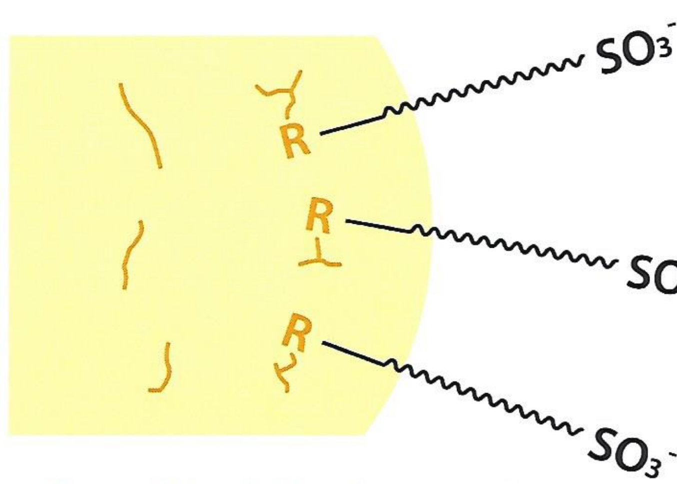
First, our polymerizable surfactants behave in a manner similar to conventional surfactants during an emulsion polymerization process in terms of providing emulsification of the monomer droplets, nucleation of polymer particles, and stabilization of these particles. Second, by the surface of the reaction, HITENOL and NOIGEN can be incorporated into the polymer and be present only on the surface of the resulting latex particles so that there are little free surfactant molecules left in the aqueous phase, and desorption of surfactant molecules from the latex or migration inside the resulting polymer film is minimized.

Conventional surfactants



Physically adsorbed on polymer particles

Polymerizable surfactants



Chemically bonded to polymer particles

BENEFITS

〔1〕 **Excellent Emulsion Stability.**

〔2〕 **Low Foaming of Latex.**

〔3〕 **Enhanced Mechanical Stability of Latex.**

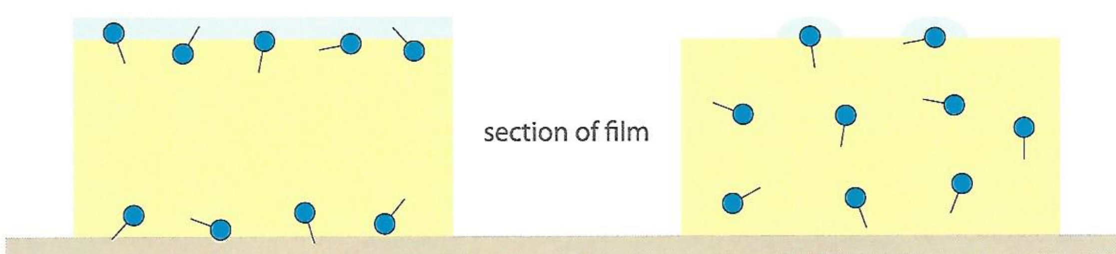
〔4〕 **Improved Water Resistance of Polymer Film.**

〔5〕 **Increased Adhesion.**

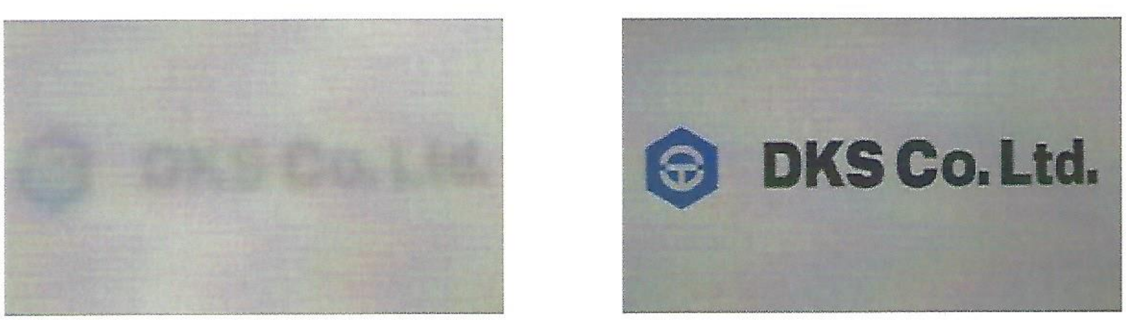
FEATURES OF POLYMER FILMS

The films made from a polymer emulsion made by using polymerizable surfactants as emulsifier, shall show higher water resistant properties of the film compared to films made from emulsions made by using conventional non-polymerizable surfactants. This is because by using polymerizable surfactants, the surfactant molecules are chemically bonded to the polymer particles, hence occurrence and migration of free surfactants are minimized.

Conventional surfactants | **Polymerizable surfactants**



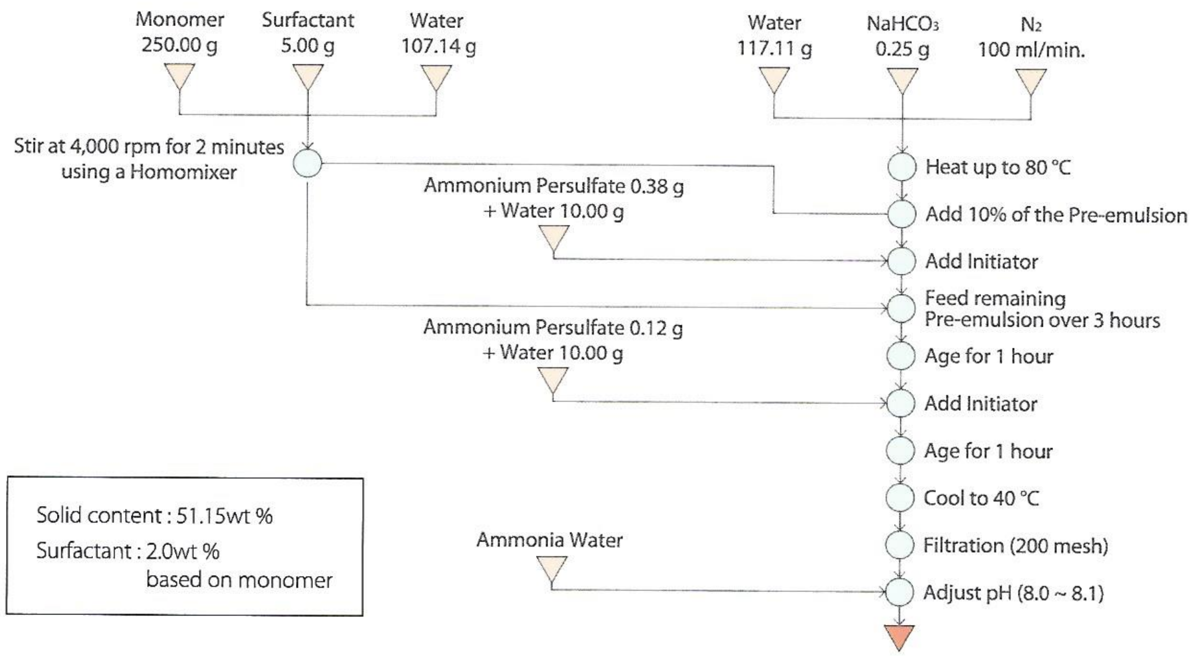
Migrating though the latex film | No migration



After immersion of Styrene / BA film in water (25℃) for 48 hours.

EMULSION POLYMERIZATION

1. MODEL EMULSION POLYMERIZATION PROCESS



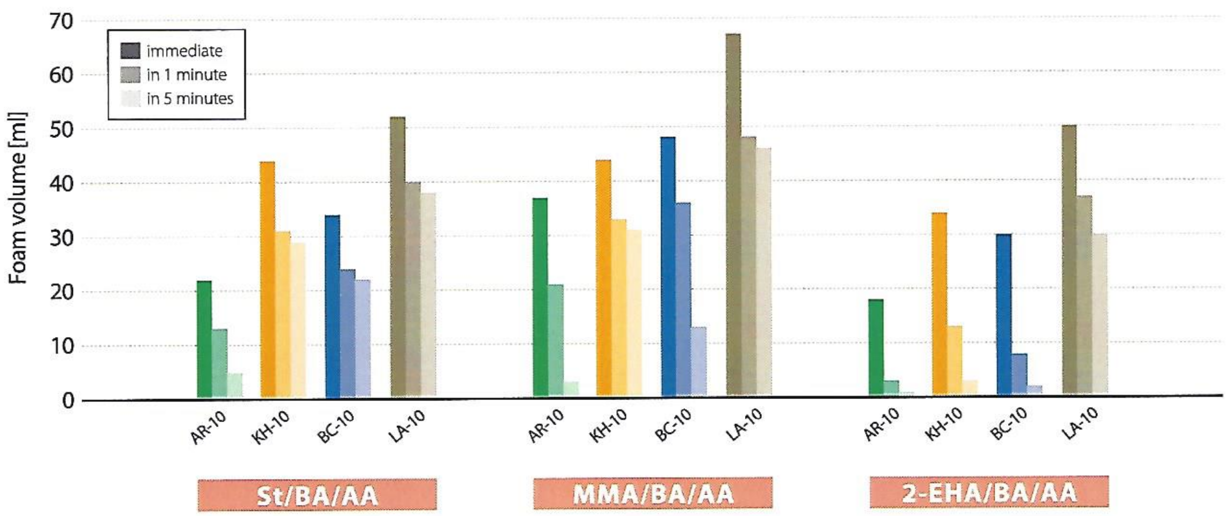
2. ITEMS EVALUATED AND METHODS

Coagulum	Weighed residual solid after filtration of emulsion through a 200-mesh screen, washed with water, and dried for 3 hours at 105 °C.
Average Particle Size	Measured by dynamic light scattering method.
Viscosity	Measured at 25 °C using BM type viscometer at 60 rpm.
Mechanical Stability	Stirred the emulsion (50 g) for 5 minutes in a Maron tester at 1,000 rpm with 10 kgf applied. Weighed coagulum after filtration of emulsion through a 80-mesh stainless steel wire screen, washed with water, and dried for 3 hours at 105 °C. Smaller values mean better mechanical stability.
Chemical Stability	10 g of various concentrations (0.1 - 6.0 mol/l) of aqueous calcium chloride was added to 10 g of the emulsion and was stirred continuously. The lowest concentration of calcium chloride solution that generated aggregates was determined. Larger values mean better chemical stability.
Conversion of Surfactants	Calculated after measuring residual free surfactants in the emulsion by ^{1}H-NMR or HPLC.
Foaming	10 g of water was added to 20 g of the emulsion in a Nessler tube at room temperature. The tube was flipped up-side-down every 1 second for 30 seconds (flipped 30 times) by hand. The volume of foam from the liquid surface was measured.
Water Resistance of Polymer Film	The emulsion was cast on a glass plate and dried for 48 hours at 20 °C, to form a 5 mil (127 μm) thick film. The glass plate was emerged in water (20 °C) for 240 hours and the color difference was measured with a colorimeter.
Adhesion	The emulsion was cast to form a 52 μm thick wet layer on a corona treated polyethylene terephthalate film of 25 mm width, and was applied to a stainless steel plate. 180° peeling test was done using a tensile tester.

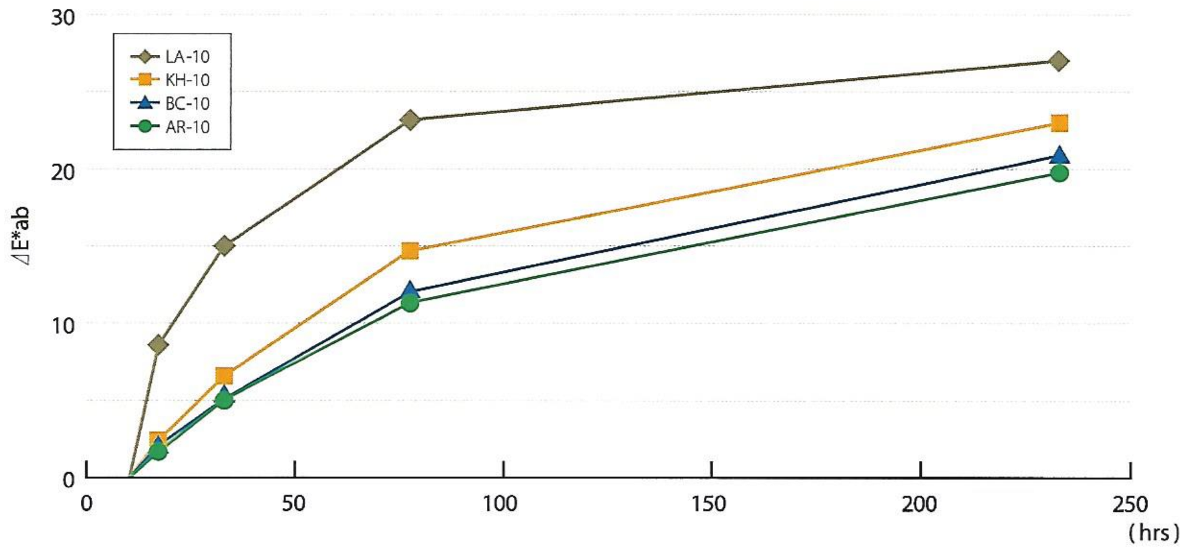
3. RESULTS

Monomer	Items Evaluated		Polymerizable Surfactants			Conventional Surfactant
			AR-10	KH-10	BC-10	LA-10[1)]
St/BA/AA[2)] = 122.50/122.50/5.00	Coagulum (Stability during Polymerization) [%]		< 0.01	< 0.01	< 0.01	0.05
	Average Particle Size [nm]		145	158	151	172
	Viscosity [mPa·s]		206	189	210	137
	Coagulum (Mechanical Stability) [%]		0.03	0.01	0.01	0.04
	Chemical Stability [mol/l]		2.0	2.0	2.0	0.5
	Conversion of Surfactants [%]		81	45	82	-
	Foaming [ml]	Immediately after	22	44	34	52
		after 5 minutes	5	28	22	38
	Water Resistance of Polymer Film (ΔE*ab)		20	23	21	27
MMA/BA/AA[3)] = 123.75/123.75/2.50	Coagulum (Stability during Polymerization) [%]		< 0.01	< 0.01	< 0.01	< 0.01
	Average Particle Size [nm]		167	176	163	172
	Viscosity [mPa·s]		352	302	360	108
	Coagulum (Mechanical Stability) [%]		< 0.01	< 0.01	< 0.01	< 0.01
	Chemical Stability [mol/l]		2.0	4.0	2.0	1.0
	Conversion of Surfactants [%]		87	92	88	-
	Foaming [ml]	Immediately after	37	44	48	67
		after 5 minutes	3	31	13	46
	Water Resistance of Polymer Film (ΔE*ab)		9	14	10	21
2-EHA/BA/AA[4)] = 123.75/123.75/2.50	Coagulum (Stability during Polymerization) [%]		< 0.01	0.01	0.01	0.01
	Average Particle Size [nm]		151	157	157	173
	Viscosity [mPa·s]		278	255	268	228
	Coagulum (Mechanical Stability) [%]		0.08	0.13	0.09	0.12
	Chemical Stability [mol/l]		0.1	0.1	0.1	0.1
	Conversion of Surfactants [%]		87	87	89	-
	Foaming [ml]	Immediately after	18	34	30	50
		after 5 minutes	1	3	2	30
	Water Resistance of Polymer Film (ΔE*ab)		20	24	21	28
	Adhesion [N/25 mm]		10.5	13.3	11.2	4.2

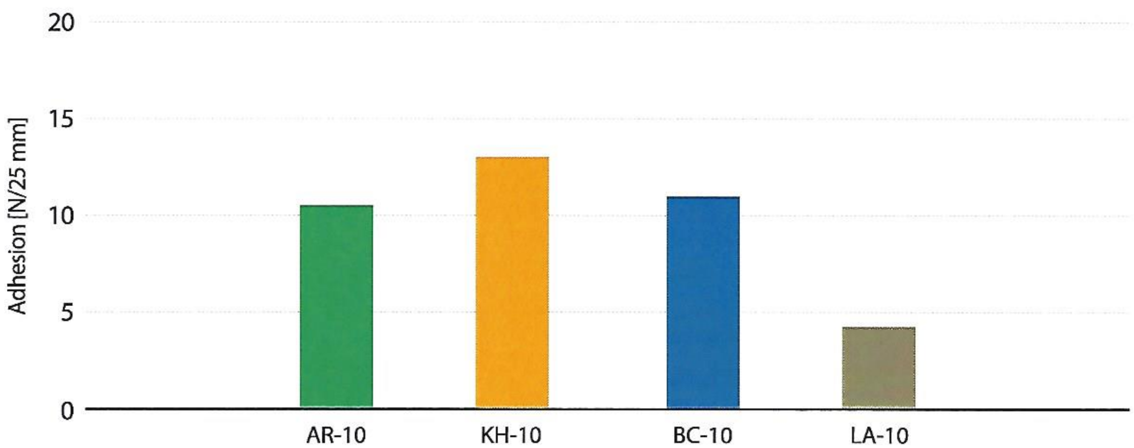
1) HITENOL LA-10: Polyoxyethylene lauryl ether sulfate ammonium salt 2) Styrene/Butyl acrylate/Acrylic acid
3) Methyl methacrylate/Butyl acrylate/Acrylic acid 4) 2-Ethylhexyl acrylate/Butyl acrylate/Acrylic acid



Foaming of latex



Water Whitening Resistance(St/BA/AA)



Adhesion(2-EHA/BA/AA)

PACKAGING

- **HITENOL AR series are available in 20 kg and 200 kg or 220 kg containers.**
- **HITENOL KH, BC and NOIGEN RN Series are available in 18 kg and 200 kg containers.**

HANDLING PRECAUTION AND STORAGE

1. **Before using these products, study the Safety Data Sheet (SDS) carefully and consult appropriate expertise, as necessary or appropriate, to become aware of and understand the data contained in the SDS and any hazards associated with the product.**
2. **Store products in tightly closed original containers at temperatures recommended on the product label and Safety Data Sheet (SDS).**

CUSTOMER NOTICE

DKS strongly encourages its customers to review both their manufacturing processes and their applications of DKS products from the standpoint of human health and environmental quality to ensure that DKS products are not used in ways for which they are not intended or tested. DKS is available to answer your questions and to provide reasonable technical support. DKS product literature, including safety data sheets, should be consulted prior to use of DKS products. Current safety data sheets are available from DKS.

1. **The data listed herein are based on experimental data obtained in the laboratory, and do not guarantee any results or performance of products.**
2. **The data listed herein may be revised without notice.**

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