Dec.4,2017

- Spinomar® NaSS -

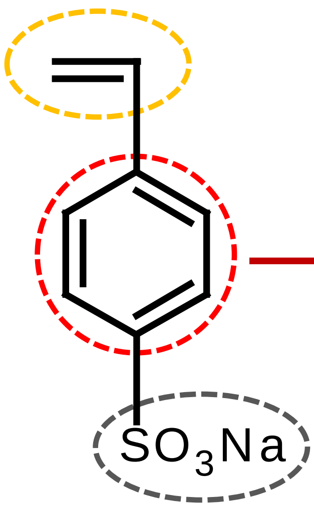
TOSOH

TOSOH FINECHEM CORPORATION

R&D

S.Ozoe

Properties of (poly)NaSS



1.Enhanced Radical Polymerizability

- conjugated by benzene ring
- e-withdrawn by $–SO_3Na$

2.Adsorption

- hydrophobicity
- π-hydrogene bonding

3.Chemical Stability

- no hydrolyzable group

4.Rigid Chain (polymer)

5.Salt & pH stability

- strong electrolyte (acidity)

Decomposition Temperature of Poly-NaSS

- Better Thermal Resistance -

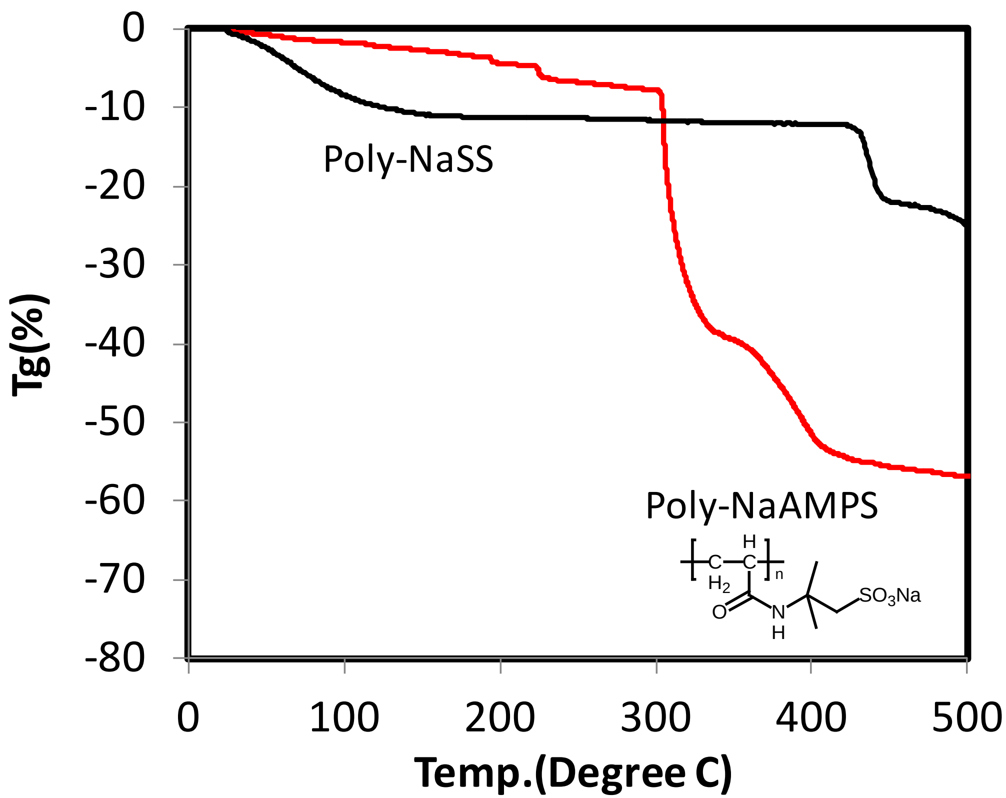


Fig. TG-DTA profile

(under N_2,10℃/min)

H_2O_2 resistance of Poly-NaSS

- Better Resistance -

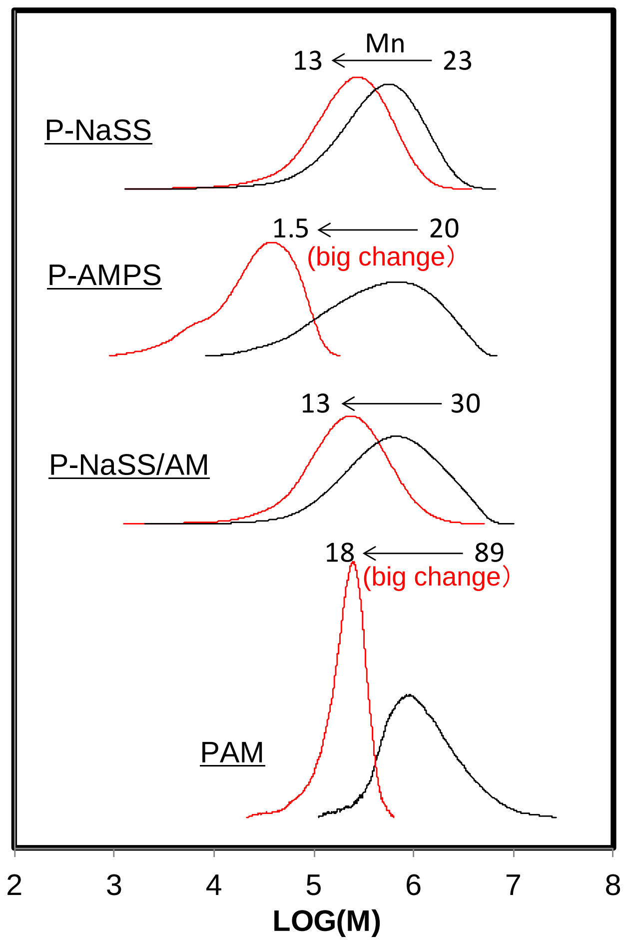
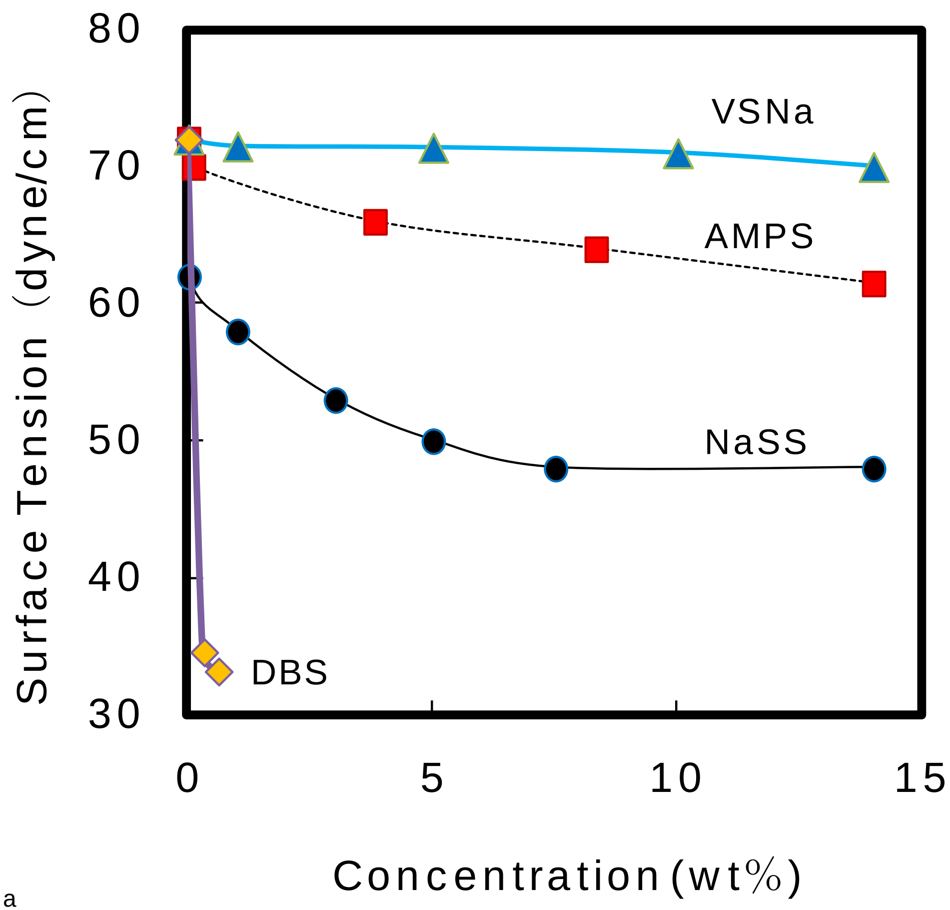


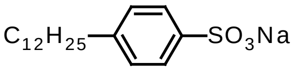
Fig. Mw(GPC) Distribution Change

(20% polym. aq.=100g/30%H_2O_2aq.=5g → 50℃×14days)

Surface activity

- More surface active -

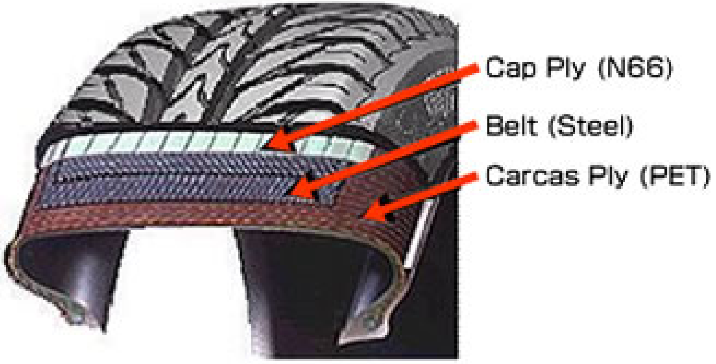




DBS

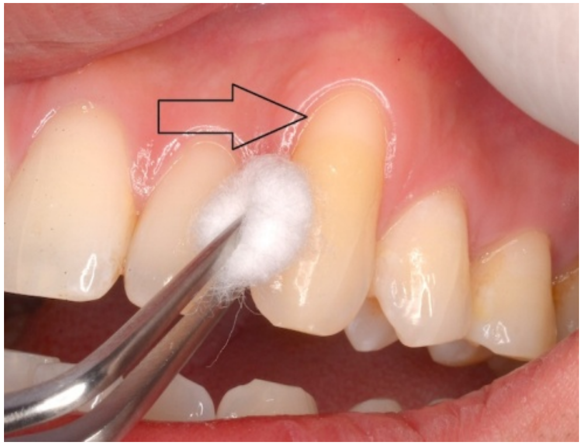
Main Application : Emulsion (Polymerization)

Emulsion Paint



Tire Cord/Rubber Adhesive

Acrylic Fiber



Remedy for teeth

Needs for emulsion paint

◆Needs (especially for architecture)

- Quick dry by high solid (filler) ⇔ High colloidal stability
- Water resistance
- Adhesion

↓

- Surfactant system is the Key

◆Reactive surfactant

- 10-20% of conventional surfactant has replaced by reactive one in Japan and 1-2% in other countries.

(The Chemical Daily of Japan,Nov.2016)

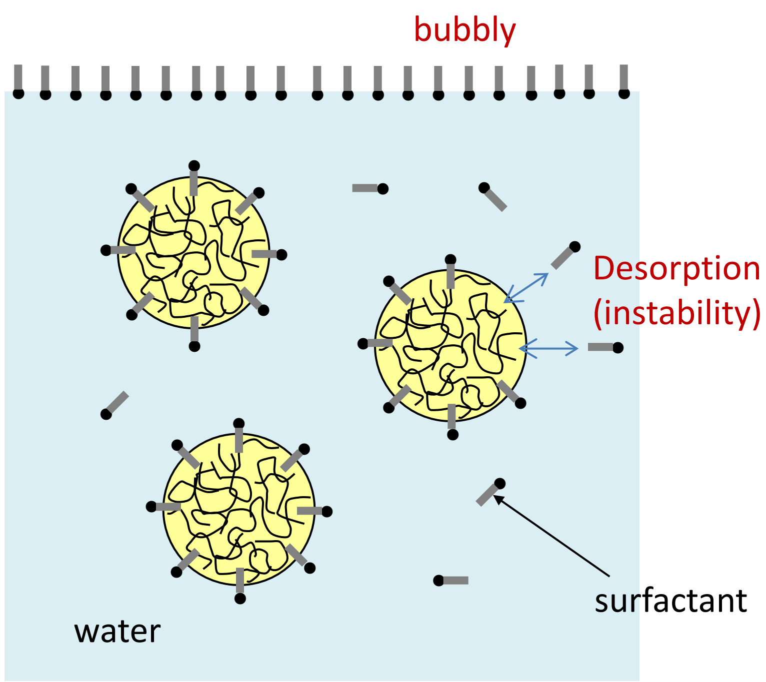
↓

◆Room for growth

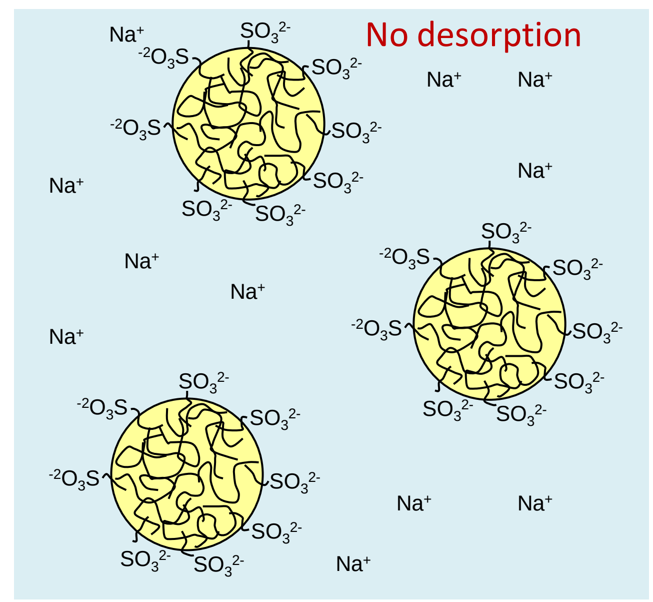
Emulsion stabilizing system

Hydrophobic monomer
Surfactant
Water

→ Initiator / Radical polymerization → Polymer Emulsion

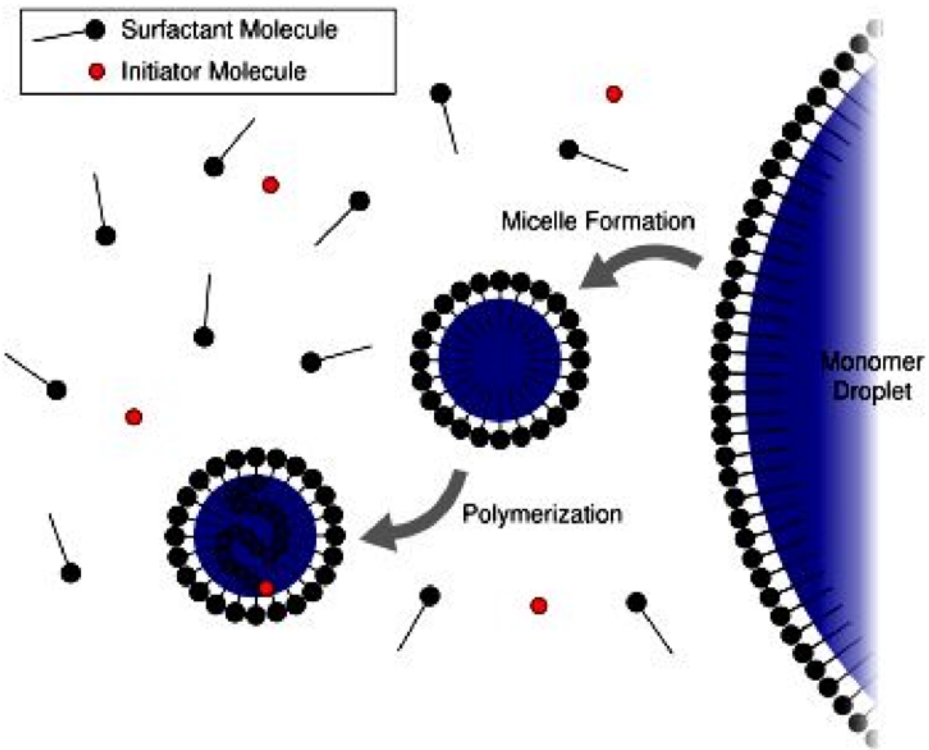


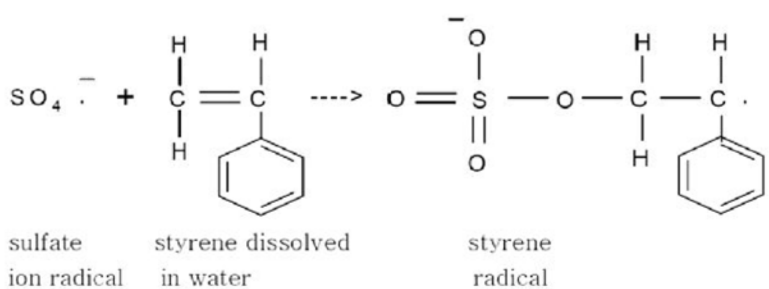
Stabilized with conventional surfactant



Stabilized with reactive surfactant

Emulsion Polymerization

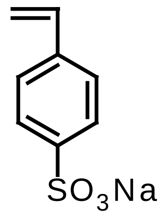
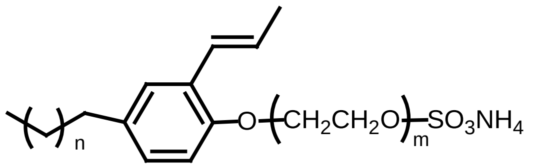
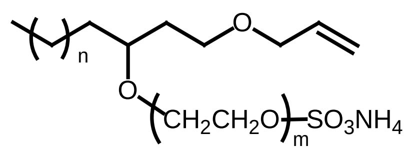




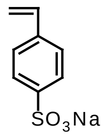
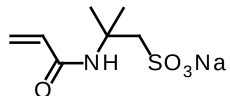
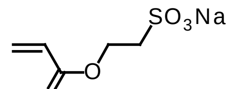
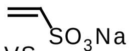
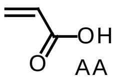
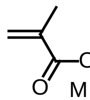
Features
- **Heterogeneous system**
- **Nucleation site: water (in micellar or homogeneous)**
- **~20nm – ~1μm**
- **Monodisperse**
- **Polymerization time: fast**
- **High MW**
- **Surfactant-free is possible**

Components
- **Monomers**
- **Water**
- **Water-soluble initiator**
- **Surfactant**

Advantages of NaSS (1/2)

	NaSS	Example of Reactive Surfactant
		 
Surface Activity	Good	Excellent
Polymerizability	Excellent	Poor
Heat Stability	Excellent	Poor
Other	Compact Molecule	･decrease adhesion ･buried into particle during Em.polym.

Advantages of NaSS (2/2)

	Sulfonate Type				Carboxylate Type	
		 AMPS	 SEA	 VS	 AA	 MAA
Acidity (pH stability) (Salt stability)	High (Strong Electrolyte)				Low (Weak Electrolyte)	
Hydrolytic Stability	Excellent	Fair	Poor	Excellent		
Heat Stability	Excellent	Good				
Polymerizability	High			Low	High	
Surface Activity	Good	Poor				
Solubility	Poor	Fair			Good	

Favorable for Emulsion polymerization but.....

Points to Note

1.NaSS sometimes reacts too fast in water phase and forms water soluble polymer (= decrease water resistance).
→ dosing condition, initiator system

2.NaSS incorporation changes significantly by initiator system, monomer/surfactant composition and dosing condition.

3.Excess Na sulfonate decreases water-resistance of polymer film.
→ appropriate quantity

4. NaSS incorporation is limited (<5%) due to its oil insolublility.

Colloidal stability increases by introduction of NaSS

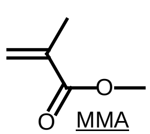
[Quoted from Jose M.Asua : European Polymer Journal 93 (2017) 480-494]

MMA/n-BA=1/1wt.r

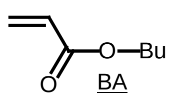
	Basic Characteristics of Latex				Salt Tolerance [Coagulation(%)]			Freeze Thaw Stability [Z-ave change(%)]	
NaSS (wt%/MM)	$-SO_3Na$ (mmol/kg)	Surface Tension (mN/m)	ζ-potential (mV)	$Z\text{-}_{ave}$ (nm)	0.02M $CaCl_2$	0.05M $CaCl_2$	1M NaCl	1st cycle	3rd cycle
3.6	86	51.8	58.4	281	<6	<6	<6	<6	
1.3	31	54.8	52.8	241	<6	massive coagulation			
1.0	24	58.1	52.6	251	<6				
0.5	12	63.3	51.0	250	<6			massive coagulation	
SDS=1.2	21	40.9	46.6	255	19				

$C_{12}H_{25}—O—SO_3Na$

SDS



MMA



BA

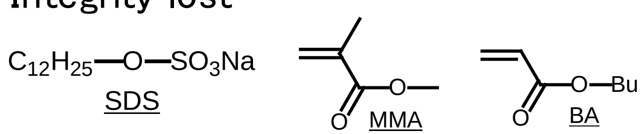
NaSS stabilized emulsion gives clean film surface

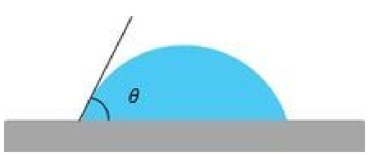
[Quoted from Jose M.Asua : European Polymer Journal 93 (2017) 480-494]

MMA/n-BA=1/1wt.r

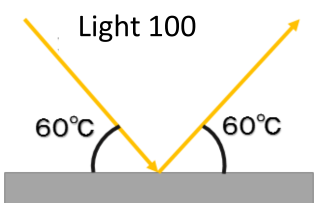
	Contact Angles			Moisture Permeability ($g\cdot mm/m^2$)
NaSS (wt%/MM)	Before Washing	After Washing	Gloss at 20°	
3.6	32.5	–*	66.4	-
1.3	68.4	69.4	64.3	59
1.0	71.1	69.7	69.1	14
0.5	69.8	69.9	66.1	10
SDS=1.2	52.4	68.3	56.3	11

* Integrity lost





Contact Angle θ



Gross

Surface is covered with SDS
(=white area)

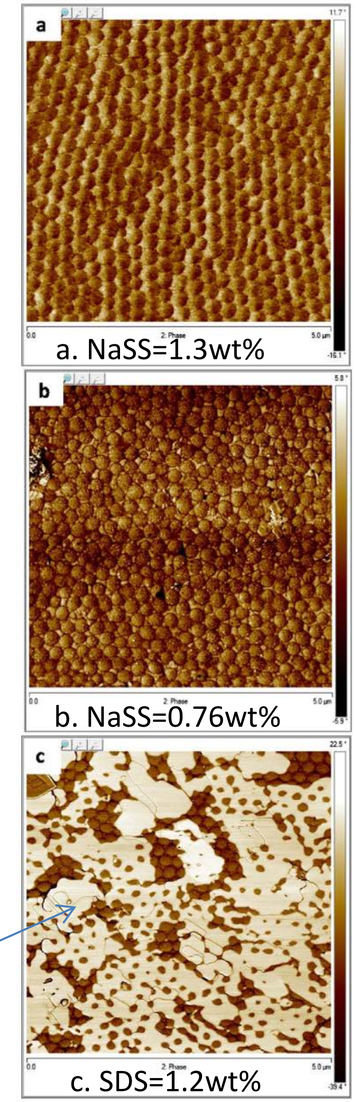


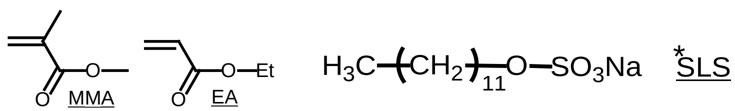
Fig. AFM phase images of film-air interface

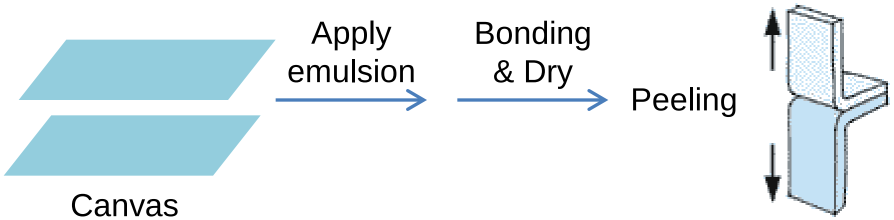
Clean surface gives better adhesion

[Quoted from M.Okubo : J. Adhe.Soc.Jap. Vol.18(4),1982,153-158]

MMA/EA =1/1 (20wt%)
NaSS/SLS* (3wt% per monomer)
Water
$K_2S_2O_8$-$Na_2S_2O_3$-$CuSO_4$

70℃×5h → Emulsion





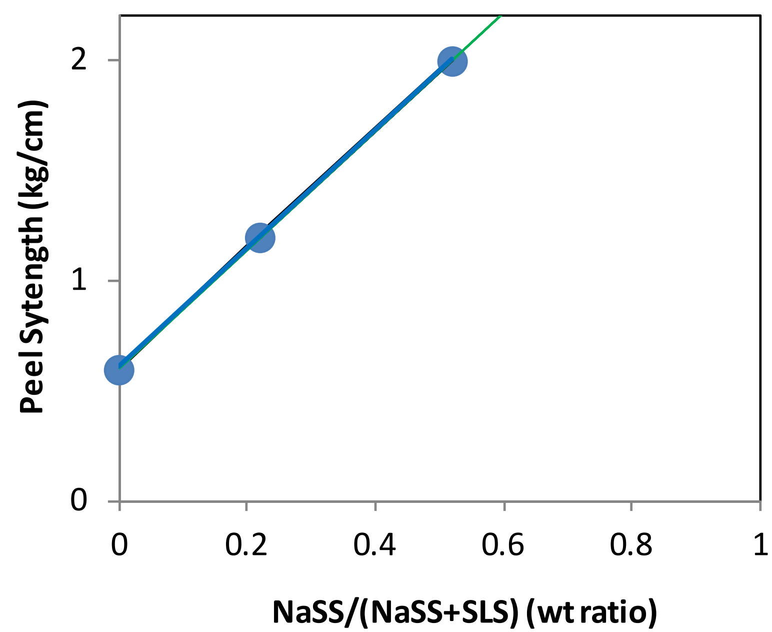


Fig. Effect of NaSS on Peel Strength

Water resistance improves by NaSS dosing condition

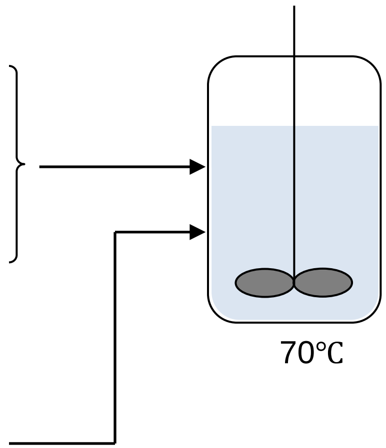
[Quoted from M.Okubo : J. Adhe.Soc.Jap. Vol.18(12),1982,530-535]

Initial Dose

St/n-BA=1/1 wt.r
(A)NaSS=1mol%×100 ~ 0%
Deionized Water
Azo-Initiator

2nd (Stepwise) Dose

(B)NaSS=1mol%×0 ~ 100%



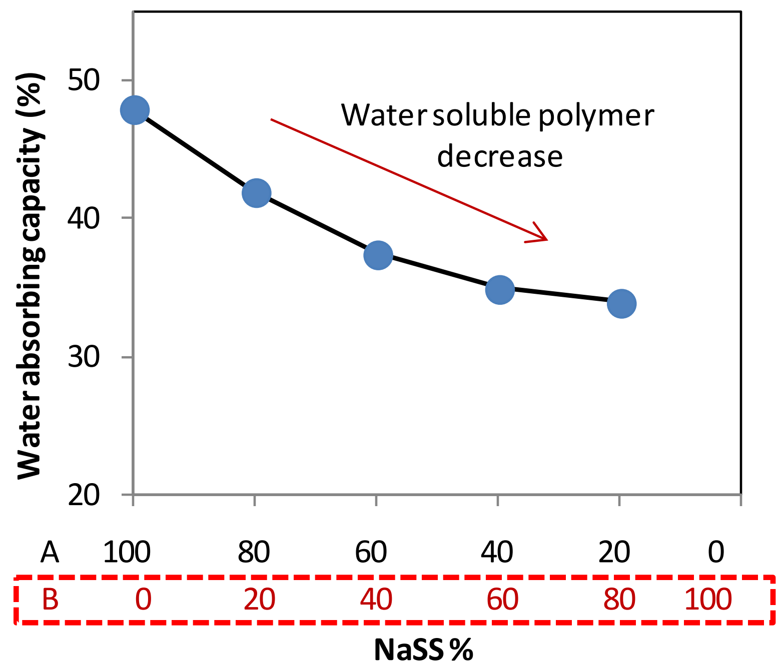


Fig. Effect of NaSS dosing condition on the water absorbing capacity of film(30℃×72h)

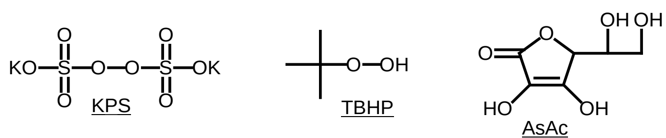
NaSS incorporation is affected by initiator system

[Quoted from Jose M.Asua : Polymer 117 (2017) 64-75]

MMA/n-BA=1/1wt.r

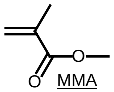
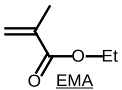
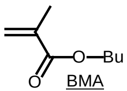
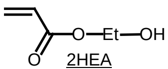
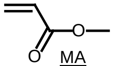
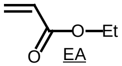
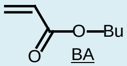
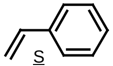
	Basic Characteristics of Latex			Salt Stability [Coagulation(%)]		Freeze Thaw Stability [Z-ave change(%)]	
Initiator System	NaSS Incorporation (%)	Particle Size(nm)	Coagulation (wt%)	0.02M $CaCl_2$	0.5M NaCl	1st cycle	3rd cycle
KPS	60.7	265	1.9	Good	NG	<6	<6
H_2O_2/AsAc	64.1	250	0.7	NG		NG	NG
TBHP/AsAc	72.5	240	0.7	<6	<6	<6	<6

NaSS=1.3wt%/total monomer



Hydrophilic comonomer increases NaSS incorporation

[Quoted from Jose M.Asua : RSC Advances 2016,6,63754-63760]

Monomer	Solubility in Water (mM) at 25℃	Particle Size (nm)	NaSS incorporation(%)
 MMA	150	188	75.5
 EMA	45	196	57.2
 BMA	4	201	53.8
 2HEA	∞	476	99.7
 MA	650	193	86.9
 EA	150	194	77.6
 BA	11	211	48.7
BA/2HEA=95/5mol%		193	78.9
 S	3.5	197	42.3

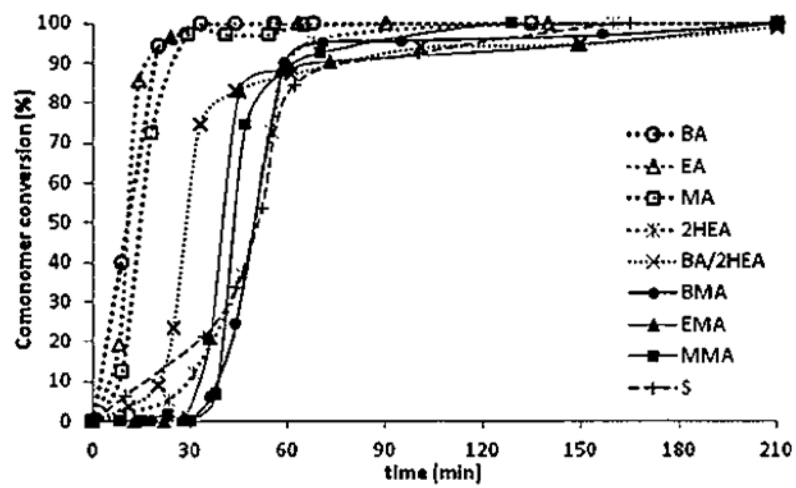


Fig. Time vs Monomer Conversion

Emulsion Paint

(US2012/58277)

★Excellent Colloidal Stability

Water
Anionic Soap
→ Reactor

<1st-MM emulsion>
Phosphorous acid-MM
n-Butylacrylate
Methyl methacrylate
NaSS
Water
Anionic Soap
→

APS →

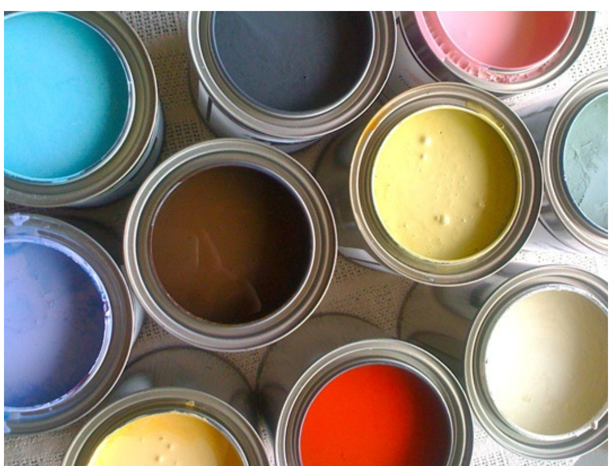
Multi-step polymerization

APS →

← <2nd-MM emulsion>
n-Butylacrylate
Methyl methacrylate
Ureido methacrylate
Water
Anionic Soap

↓

Emulsion



Acrylic Fiber : Dyeing Site

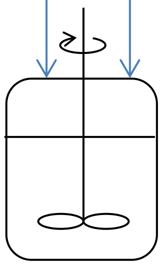
(JP57-10613)

★Distribution of -SO_3Na group
★Spinning behavior (less void)

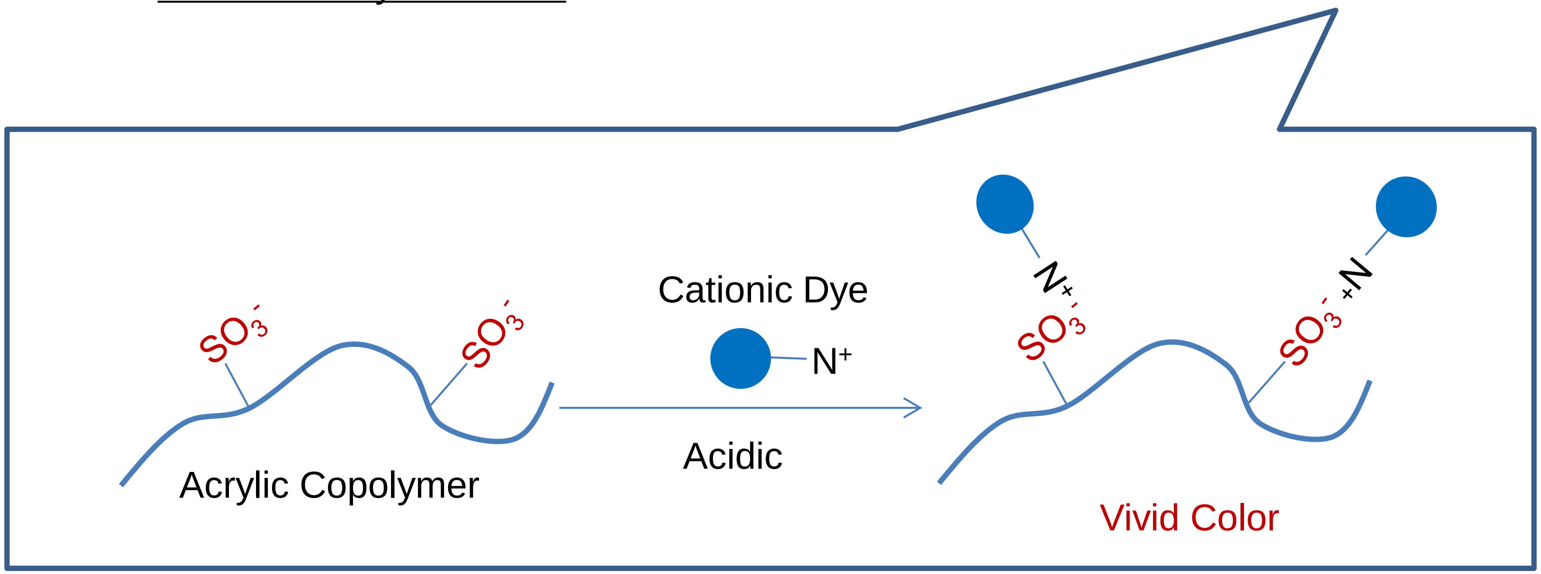
Monomer Emulsion
- Acrylonitrile
- Vinylchloride
- NaSS*

(*stepwise dosing)

Radical Initiator
Other Additives



Emulsion Polymerization → Salting out → Dissolving → Spinning → Acrylic Fiber → Dyeing



Acrylic Fiber

- Strong demand for flame retardency of acrylic fiber
  - addition of flame retardant → decreasing properties,drop out of retardant
  - copolymerization of VCM/VDC → decreasing transparency
  - copolymerization of NaSS → easy for AN≧85%,hard for modacrylic

⇩

- Improvement of NaSS feed condition（=decreasing void）（JP58-91710）

  AN=40～65wt%
  VCM or VDC=31～59.9wt%
  NaSS=0.1～4wt%
  surfactant=0.2～5wt%

（example recipe）

AN=10.8 parts
VDC=8.2
VCM=46.1
Na lauryl salfate=0.9
water=260
APS
sodium bisulfite

AN=29.6 parts
VDC=4.6

APS

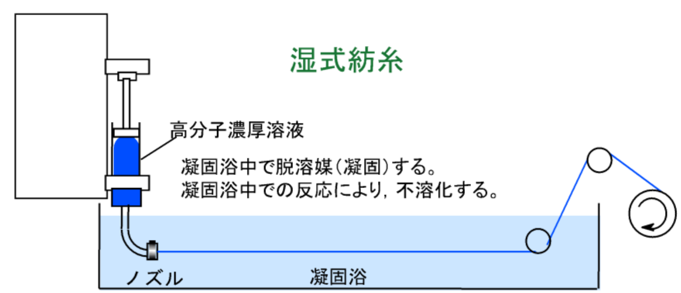
38℃×7h、pH=2.2

2h — 6h

NaSS=0.7parts

Salting out/dissolving → spinning →

Prevent a decrease in strength due to the generation of voids or agglutination in the fiber



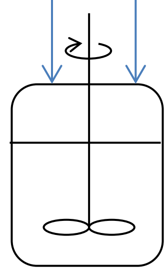
Latex Adhesive for tire cord(PET)

(JP4786061)

★Excellent
Colloidal & Heat Stability
Adhesion（130 ,170°C curing）

Monomer
- NaSS (0.1)
- 2-Vinylpyridine (7.5)
- Styrene (35.1)
- Butadiene (16.5)
- Glycidyl methacrylate (0.9)
- t-dodecylmercaptane (0.2)

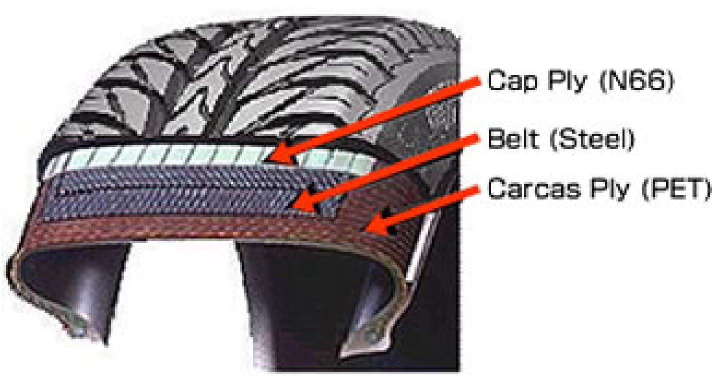
- Water (140)
- K-rosinate (1.5)
- Dispersant (1.0)
- APS* (0.3)



Conv.=80-90% → → → → Adhesive

Formulation

- K-rosinate (2.0)
- 2-Vinylpyridine (6.0)
- Styrene (6.0)
- Butadiene (28.0)
- t-dodecylmercaptane (0.4)



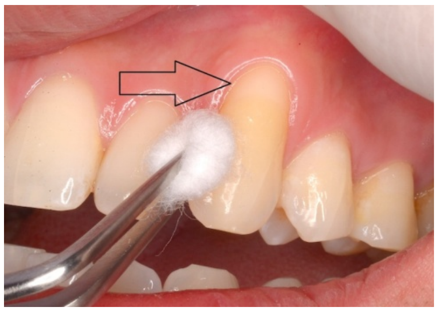
Tire=Critical Safety Parts

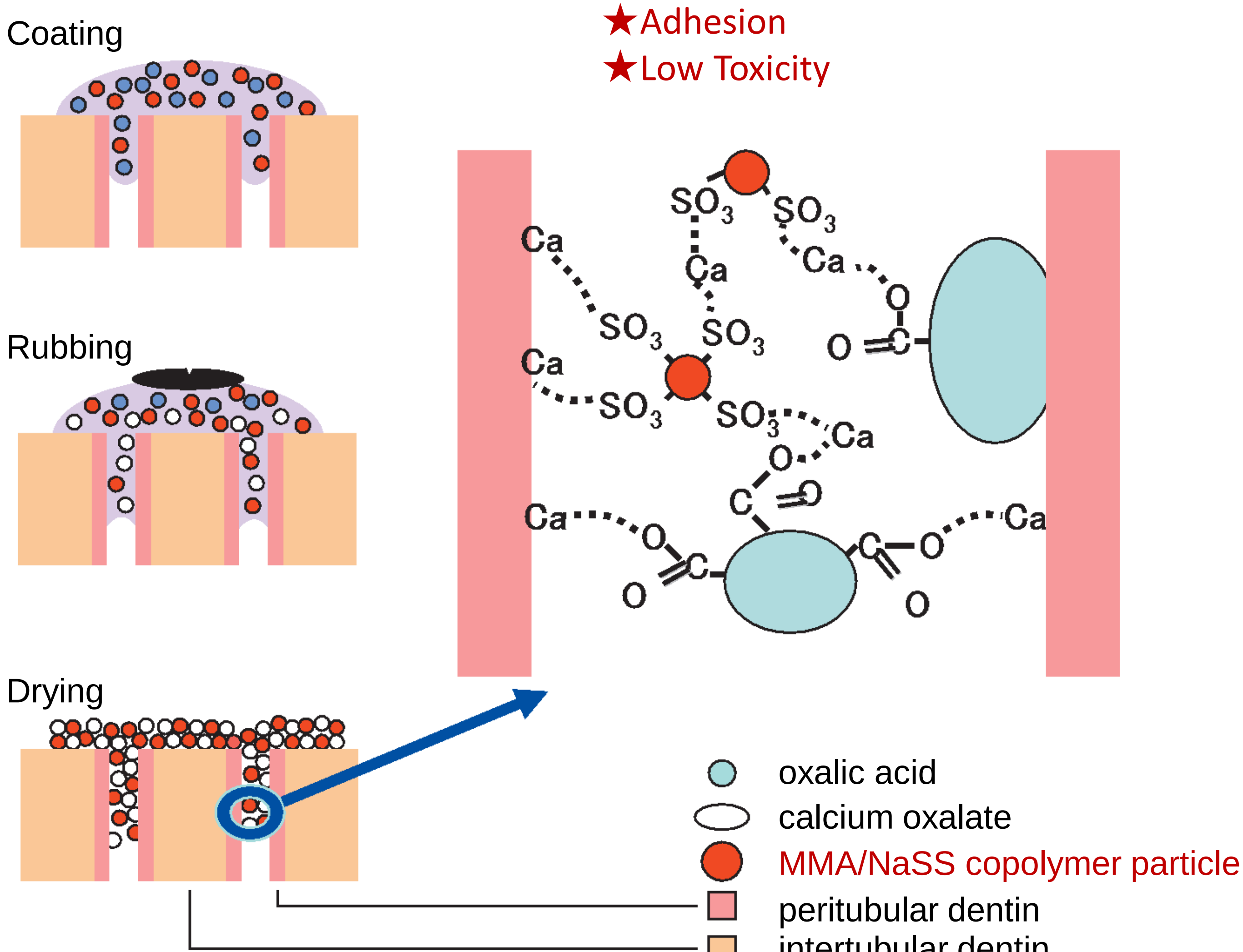
(*Ammonium persulfate)

Hyperesthesia-suppressing Agent

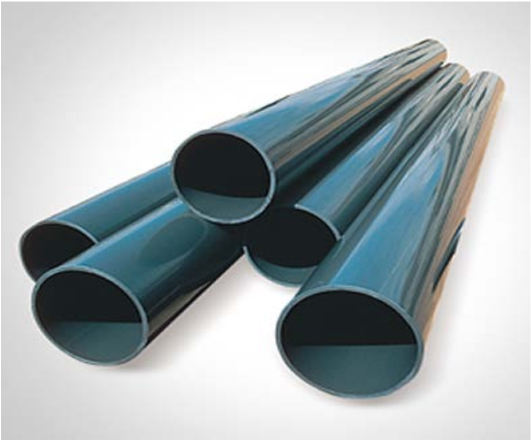
★Colloidal Stability
★Adhesion
★Low Toxicity

Protective coating using NaSS copolymer particle



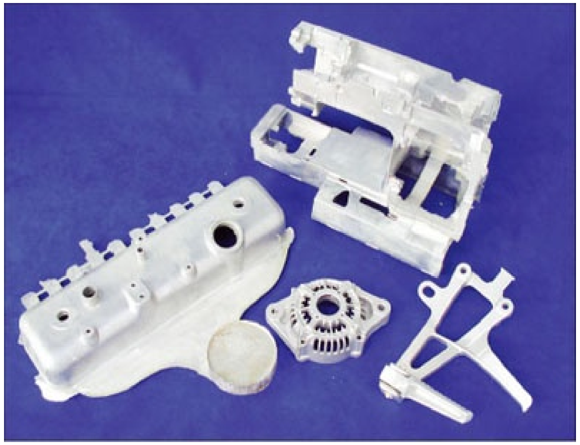


Dispersion/Dispersant



Chlorinated PVC

Agrochemical Granule

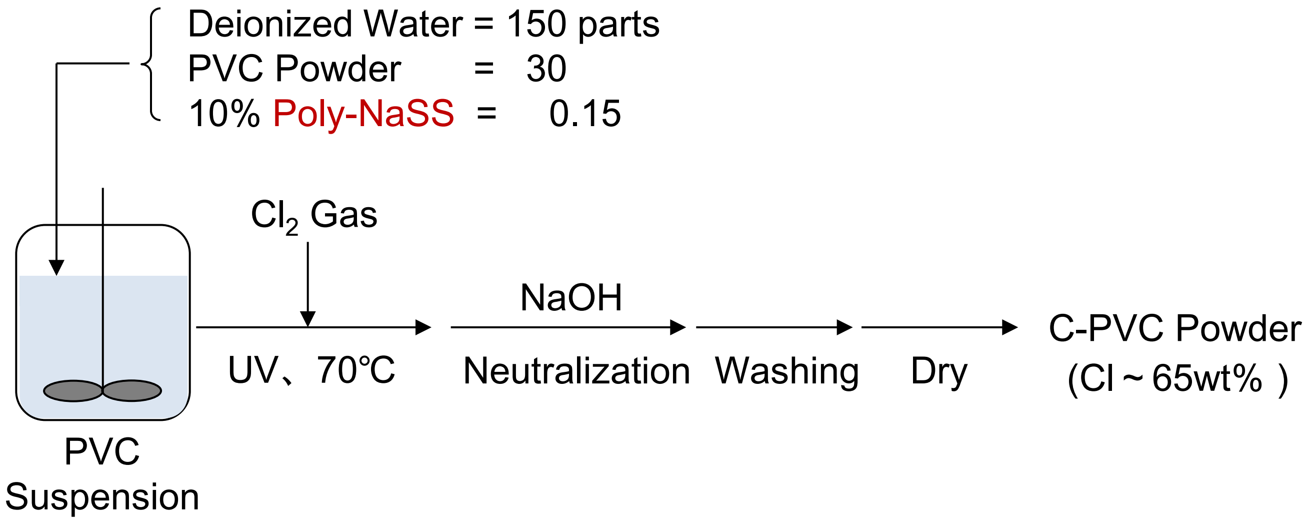


Mold Lubricant

Scale Inhibitor

Chlorinated PVC

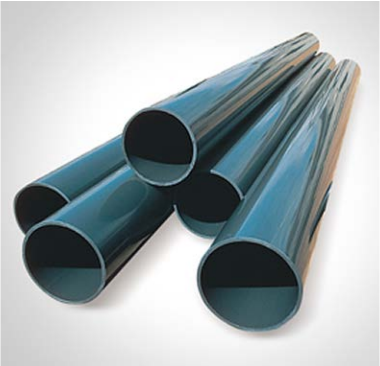
(JP3176504)



<u>Heat distortion temperature(℃)</u>
PVC = 60～ 80
C-PVC = 80～120

★Stable Dispersant

Poly-NaSS improves uniformity of the chlorination reaction.
As the result,thermal stability (=color fastness and transparency) of C-PVC improves.



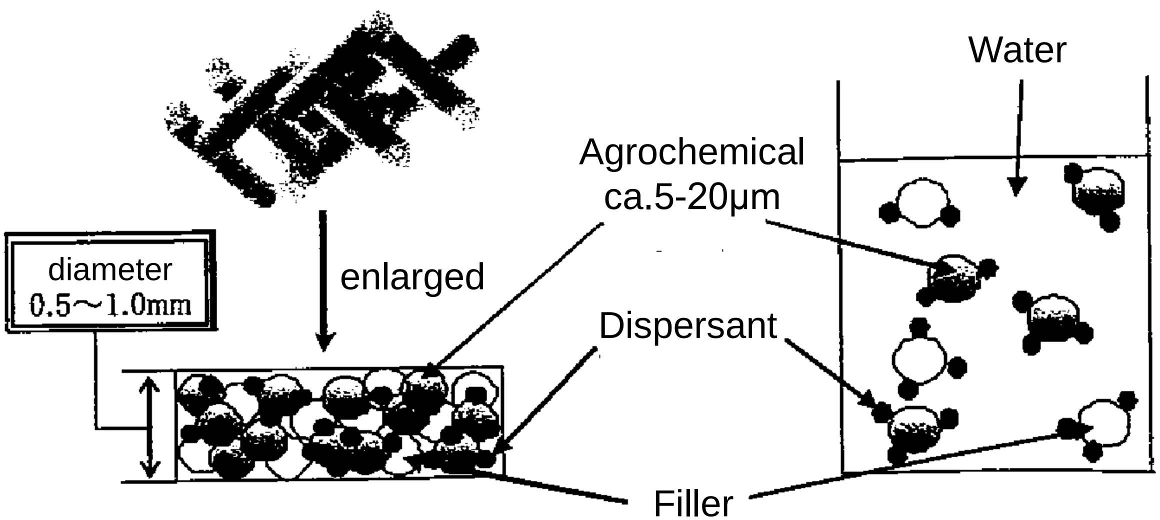
Water dispersible agrochemical granule

(JP63-236701)

★Dispersant & Binder

Agrochemical
Kaolinite clay
Poly-NaSS
Other additives
Water

→ granulation → fluidized bed drying → product

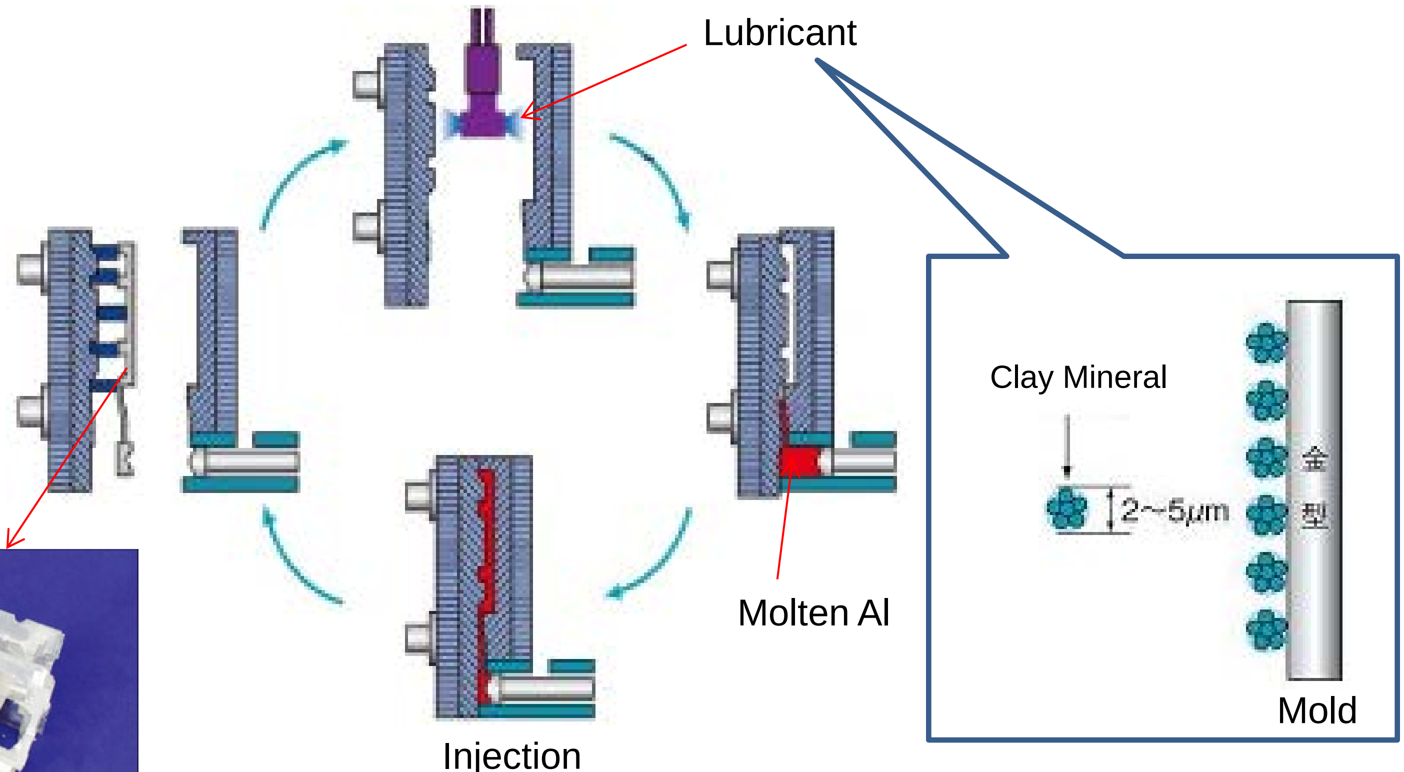


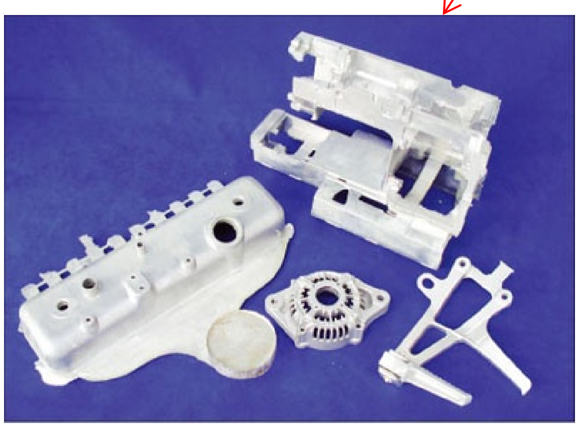
Before dilution

After dilution

Water-based Mold Lubricant

(JP4464214)





★Heat stable dispersant & Adhesion

Poly-NaSS enhances dispersion stability and adhesion (wettability) to the mold.

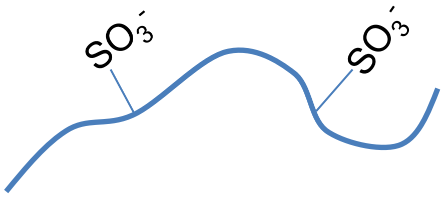
Polymeric Surfactant (dispersant)

★Dispersant & π-hydrogene bonding

NaSS

Co-monomer
  Hydrophilic MM
  Hydrophobic MM

Radical Polymerizaition



Durable to Ca^{2+},Mg^{2+} etc
Good heat resistance

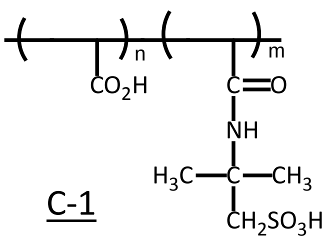
<Example Use>
- Scale inhibitor (Water Treatment,Oil Field)
- Sizing emulsion for paper (durable to hard water)
- Dispersion of pigment,silicate,CNT etc
- Washing agent , Thickener



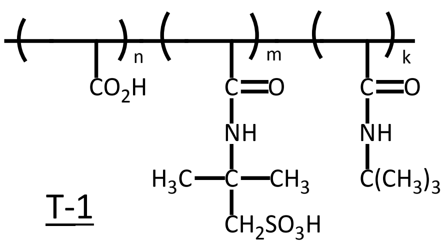

Calcium phosphate inhibitors (1/2)

[Quoted from Zahid Amjad : Phosphorous Research Bulletin,20,165-170(2006)]

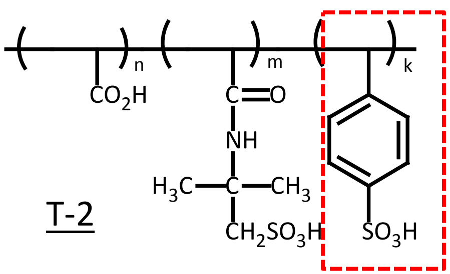
★NaSS moiety increases the heat stability of polymer.



C-1



T-1



T-2

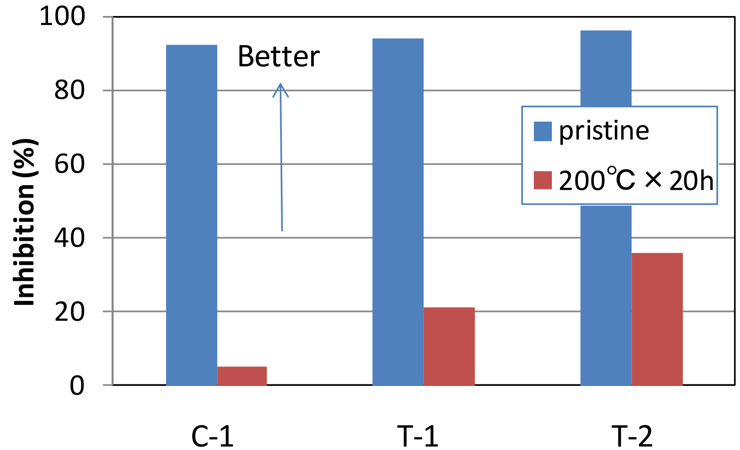


Fig. Effect of heat treatment on the polymer performance

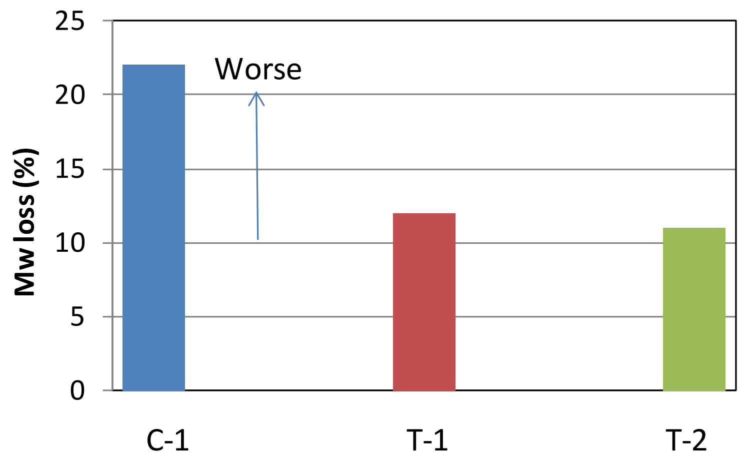
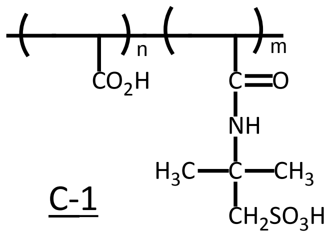


Fig. Mw loss of polymer after heat treatment

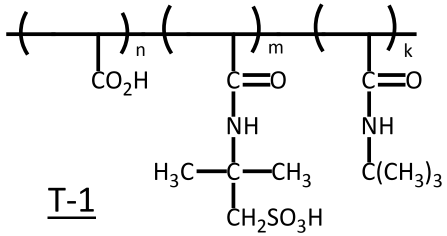
Calcium phosphate inhibitors (2/2)

[Quoted from Zahid Amjad : Phosphorous Research Bulletin,20,165-170(2006)]

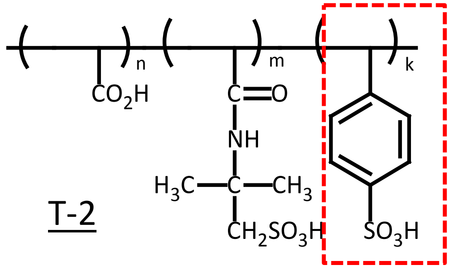
★NaSS terpolymer maintains inhibition performance after heat treatment.



C-1



T-1



T-2

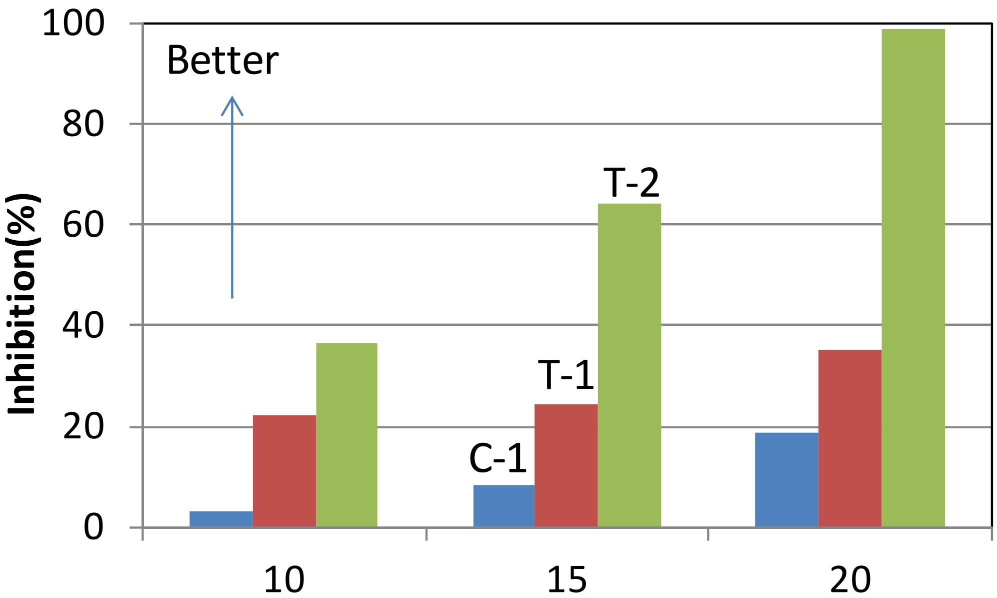
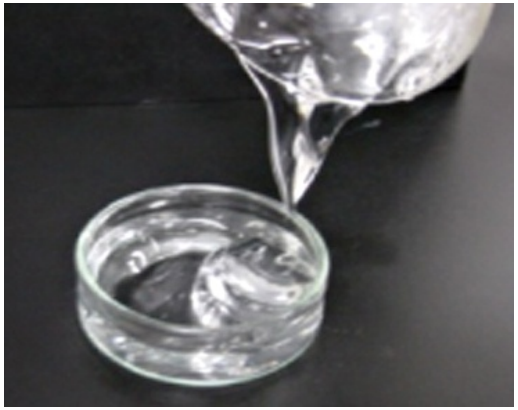


Fig. Effect of polymer dosage on the heat-treated sample

Toiletary

Ironing Aid



Thickener

Textile Washing

Advantage of POLYNASS®

★Low APHA(=good hue): protected by our Patent**

MA-2005L*	PS-1	PS-5	PS-50	PS-35*	PS-100
(APHA80)	(>250)	(>250)	(70)	(30)	(70)

*for specific customer
**(JP5946094),US9505713,TW1573781

Ironing Aid

★Poly-NaSS acts as heat-stable glue, dispersant

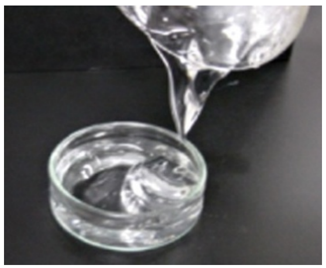
Poly-NaSS (substitute of starch)
Silicone polymer (smoothing agent)
PPG (stabilizaer)
Preservative
Flavor
Etc
Water

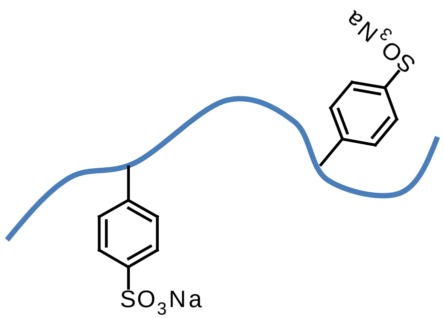
Poly-NaSS has an excellent resistance to heat and discoloration.

Aqueous thickener for bleaching detergent

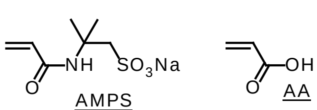
(JP4577308)

★NaSS moiety increases H_2O_2 stability of Poly-AMPS





	Polymer Composition(mol%)		
	NaSS	AMPS	AA
Polymer-A	10	40	50
Polymer-B	10	70	20
Polymer-C	-	50	50
Polymer-D	-	80	20



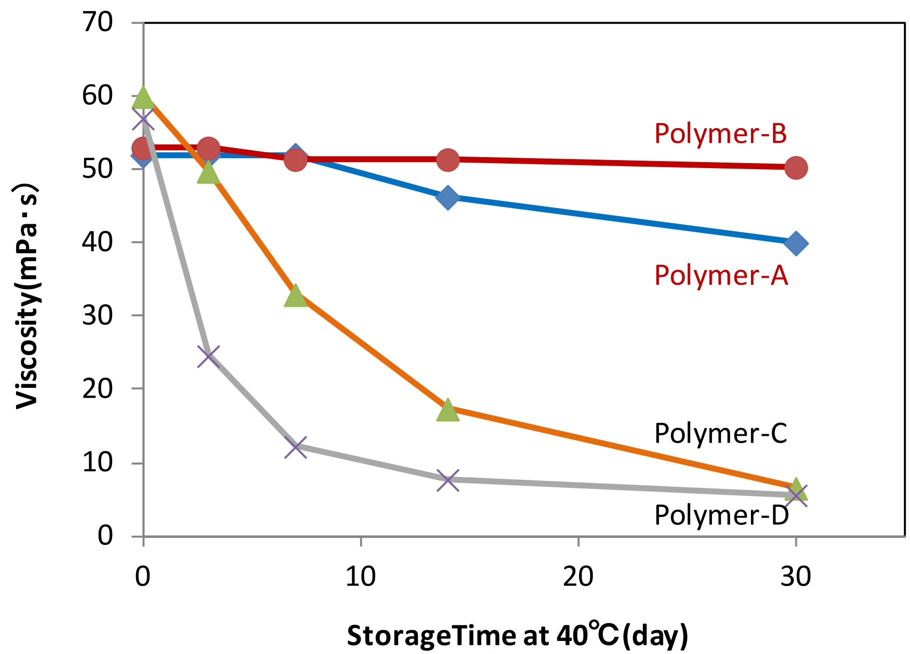
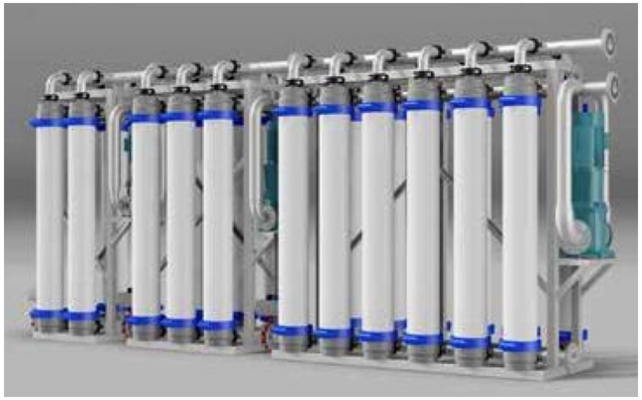


Fig. Viscosity stability of detergent composition
(Citric acid=10%,H_2O_2=0.2%,pH～2)

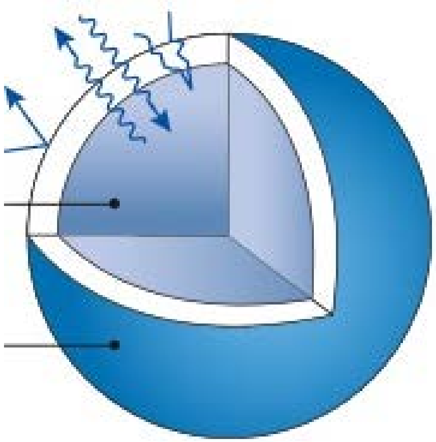
Anion/Cation Interaction (Layer-by-Layer)



Nano-filtration

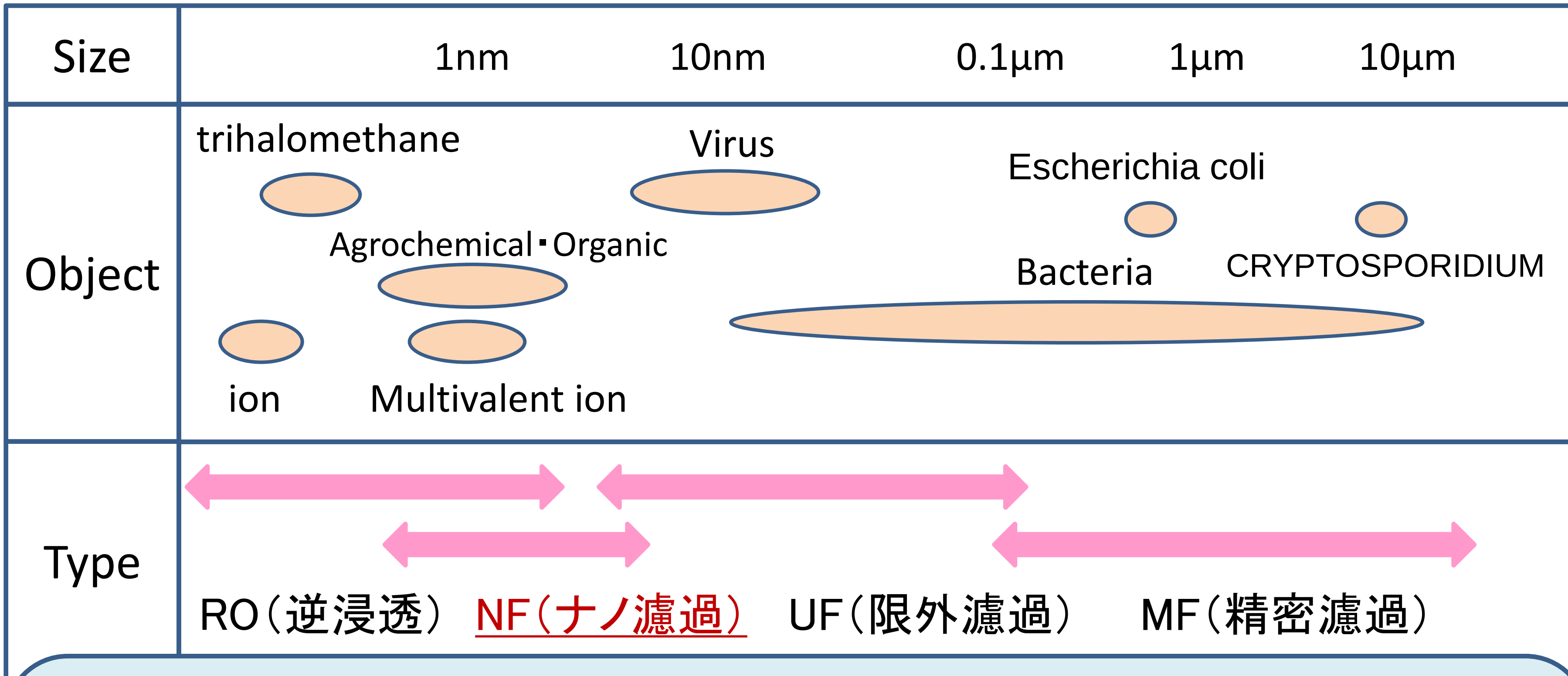
Anti-clumping

Allergen Catcher



Microcapsule

Filtration Membrane



＜Conventional Production method ＞

・Interfacial condensation

・Graft reaction using enzyme

・Radiation graft polymerization

・Chemical modification of polymer

Simplified

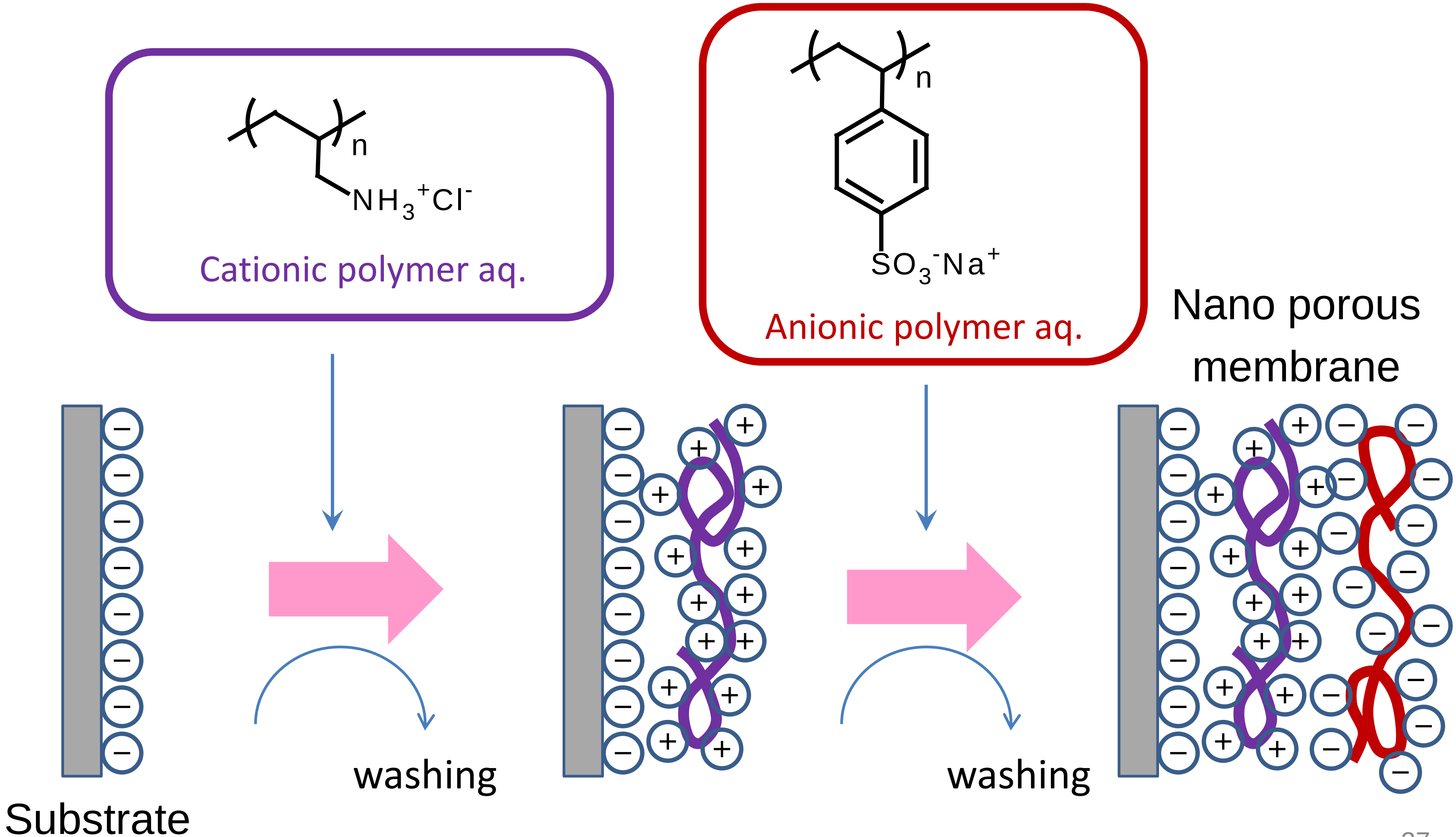
Decrease deficit

＜Layer-by-Layer＞

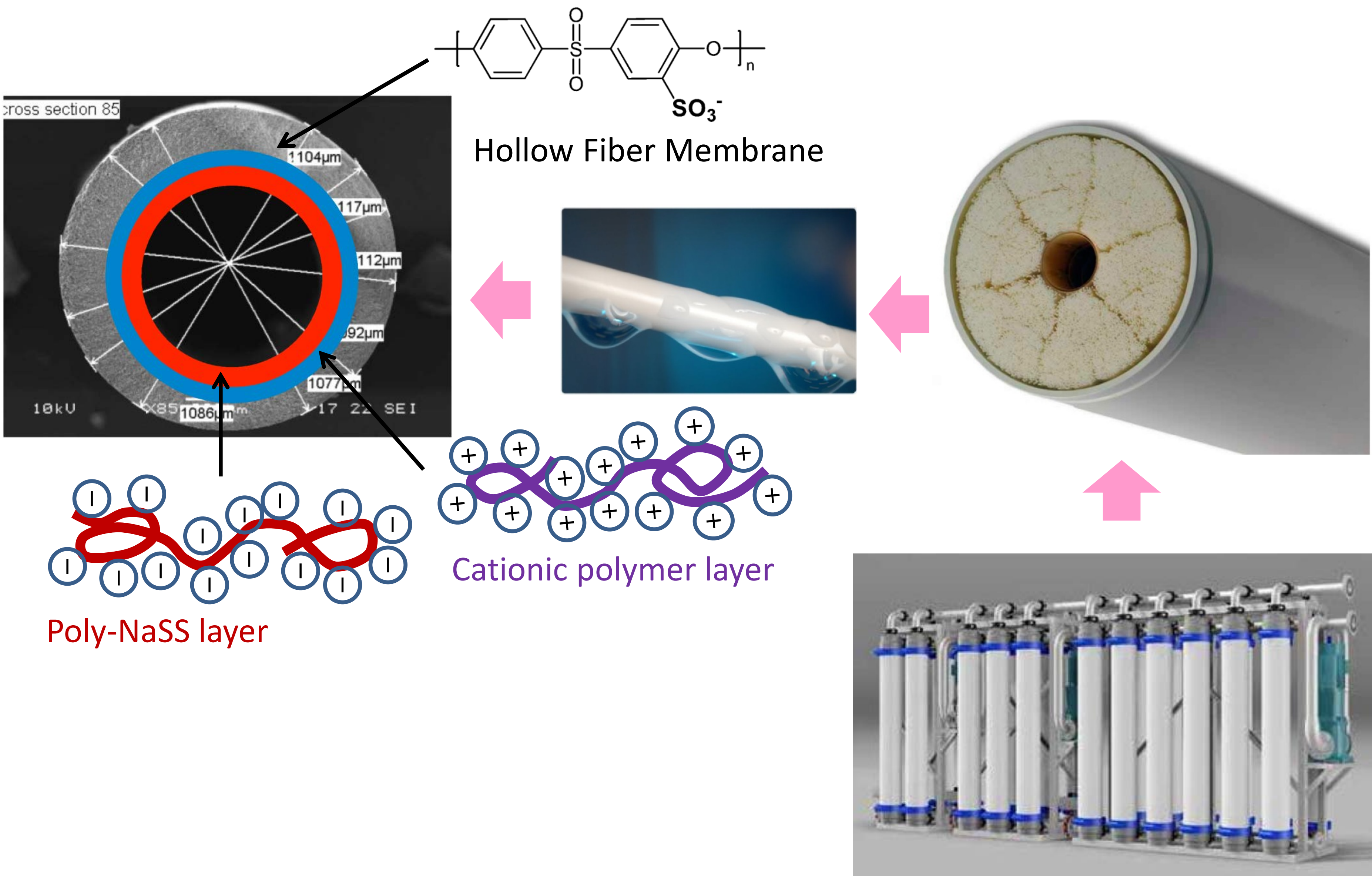
・Coating by polymer aq.

Nano-filtration by LBL technique

Very simple

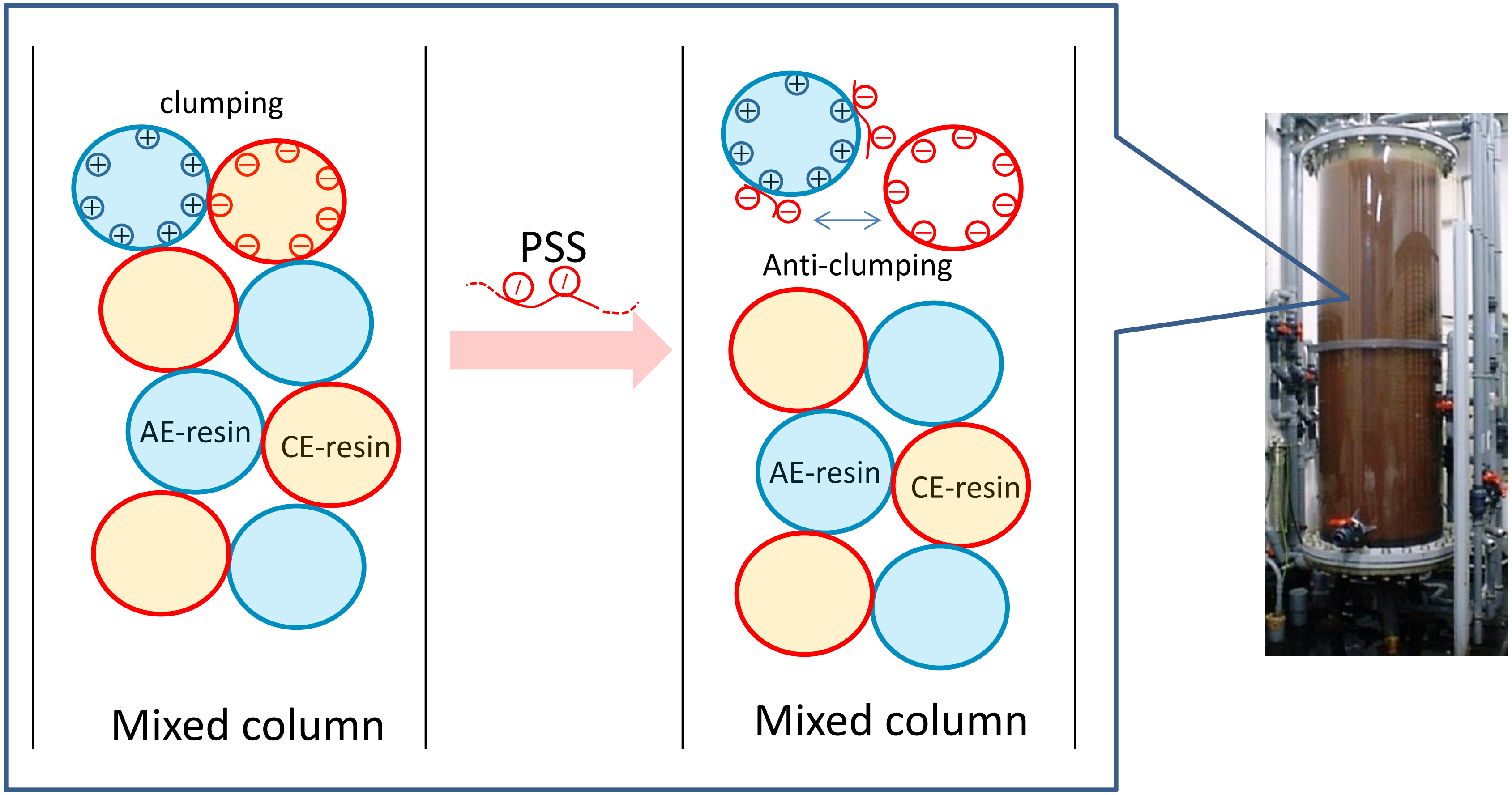


Nano Filtration Membrane



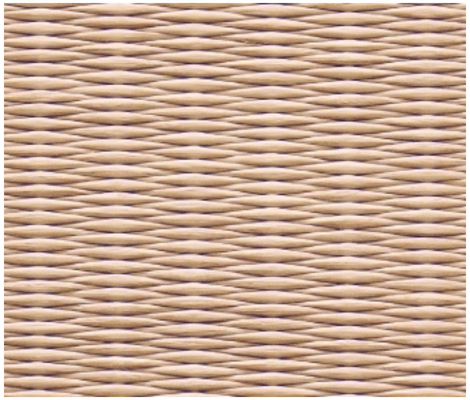
Anti-clumping of A/C-exchange resin by Poly-NaSS

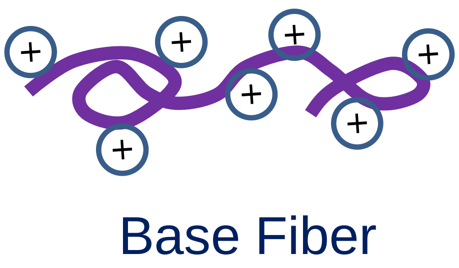
By Cation-Anion Interaction

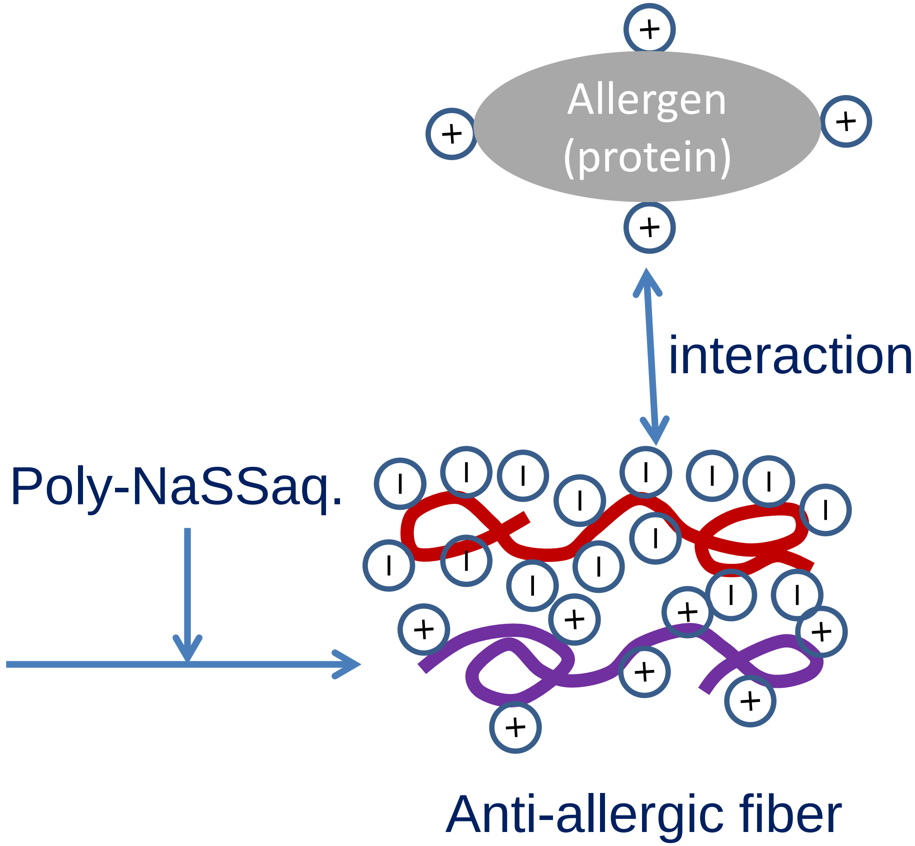


Anti-allergic Fiber

★Strong electrolyte & Adhesion



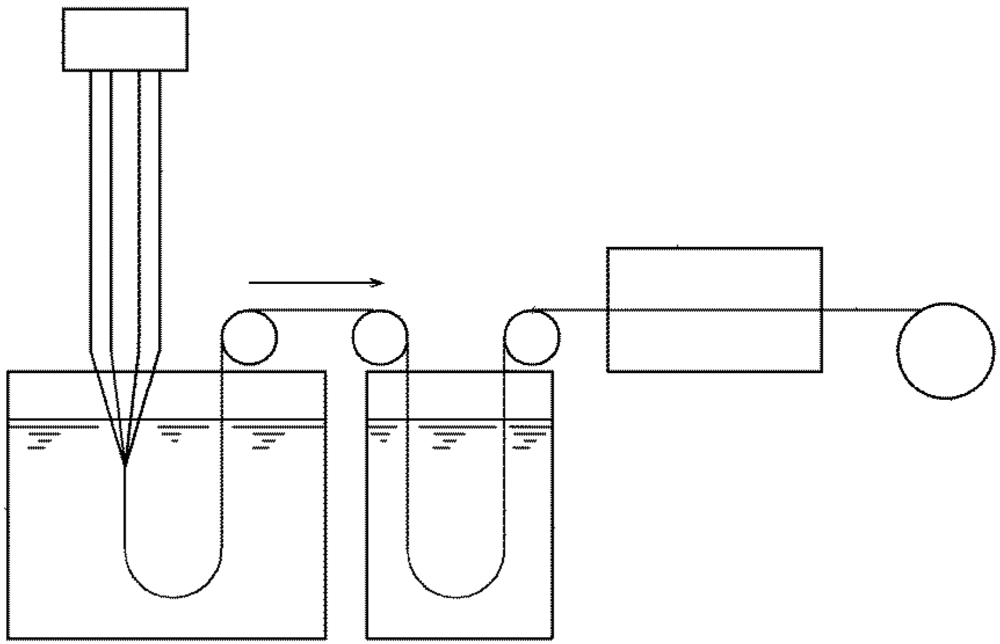




Anti-bacterial Fiber

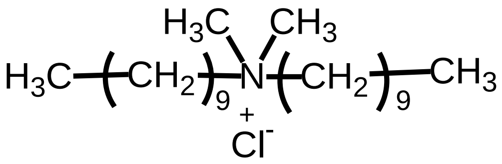
★Strong electrolyte & Adhesion

Viscose rayon aq.
(ca.5% Poly-NaSS)



Wet spinning

Dip & Dry



Anti-bacterial quaternary ammonium compounds fixed by poly-NaSS

Others

Cation Exchange Membrane

Oil Field Chemicals

Offset Printing

Biomedical Electrode

Oil Field Chemicals for harsh condition

<Application>

・Rheology Modifier

・Scale Inhibitor

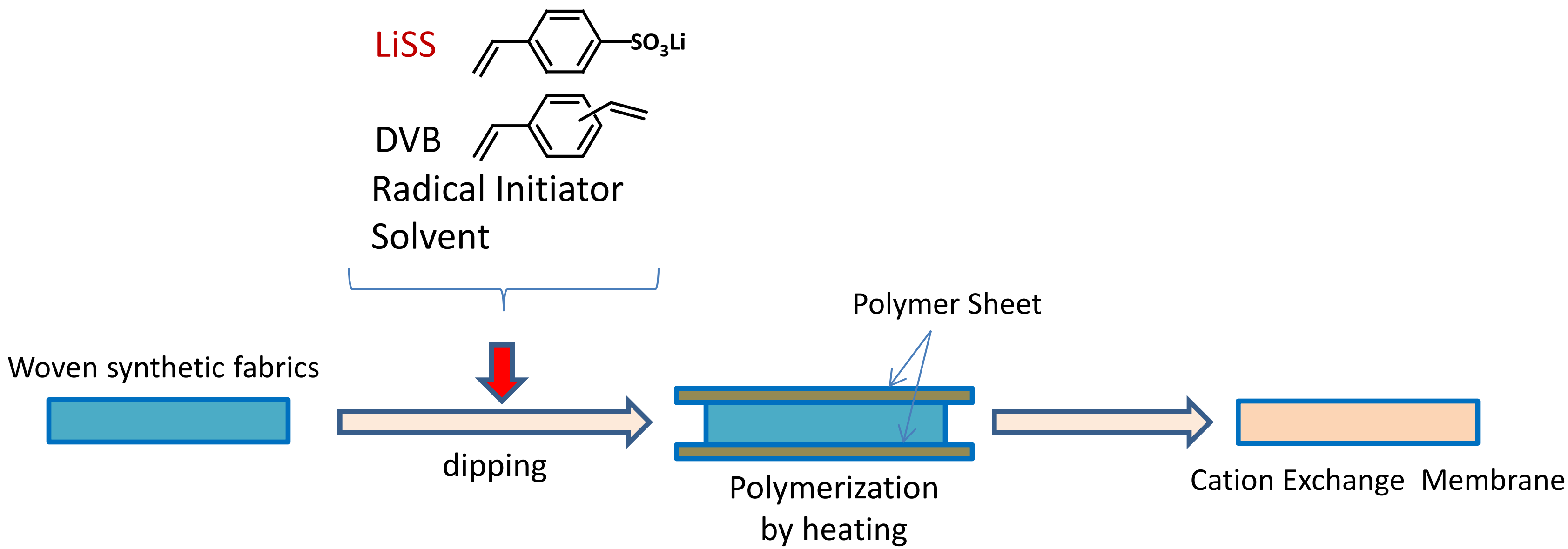
★Biggest use of AMPS

Table 1 Application of AMPS or ATBS (powder,pellets, aq.solution)

Oil Field Chemicals	EOR(UHMW Poly-AMPS by high purity grade) Fluid loss additive, Scale inhibitor etc
Water Treatment	Scale inhibitor
Textile	Acrylic fiber
Toiletary	Detergent,Skin/Hair care
Coatings	Emulsion paint
Medical	Hydrogel for biomedical electrode
Construction	Concrete formulation, Cement

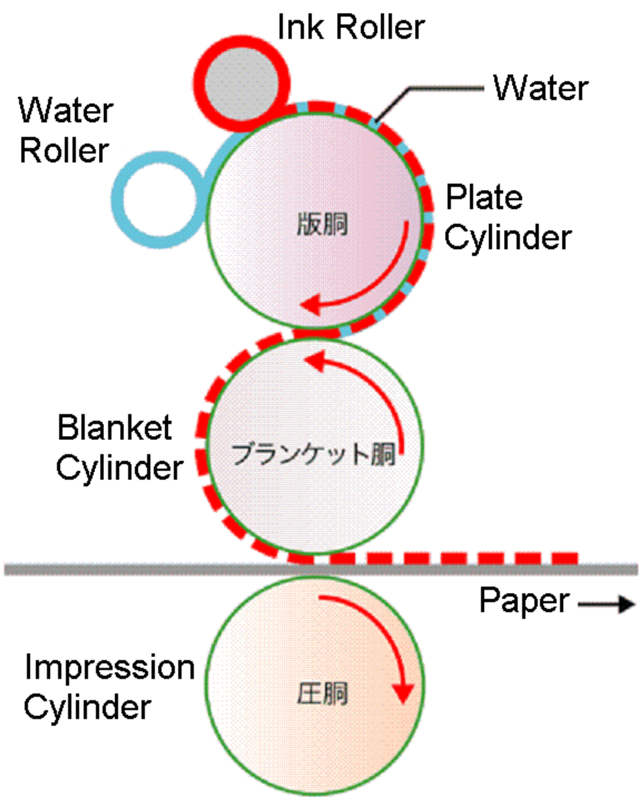
Cation-exchange Membrane

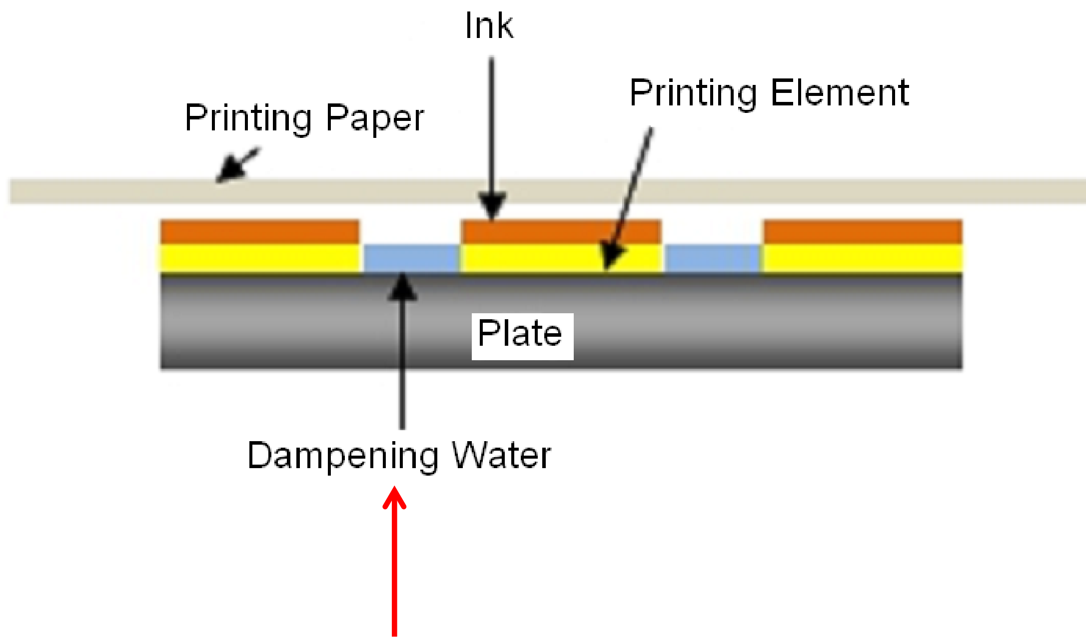
- Simple process without hazardous substances -



Dampening Water of Offset Printing

★Strong electrolyte & Adhesion



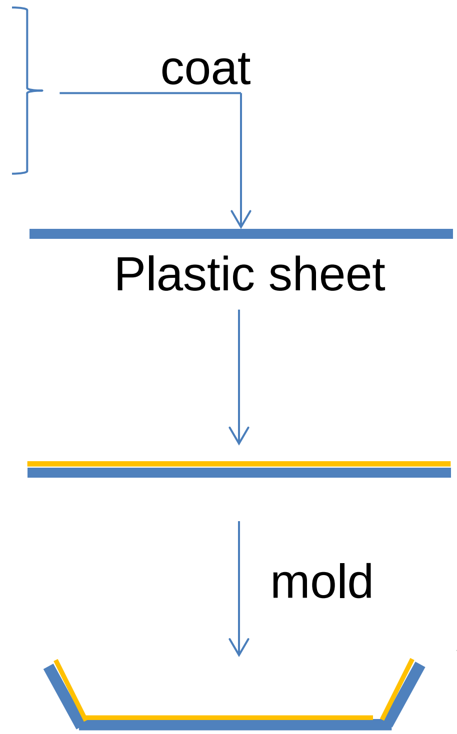


Poly-NaSS is added as an anti-statics

Anti-static plastic tray

★Strong electrolyte

Water-base binder resin
Poly-NaSS or NaSS monomer aq.
Other additives



Surface resistance $<10^{10}$

Tray for carrying semiconductor

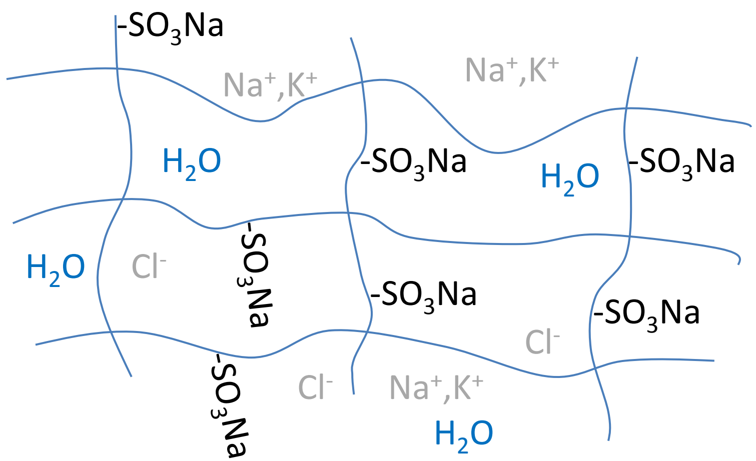
Biomedical Electrode

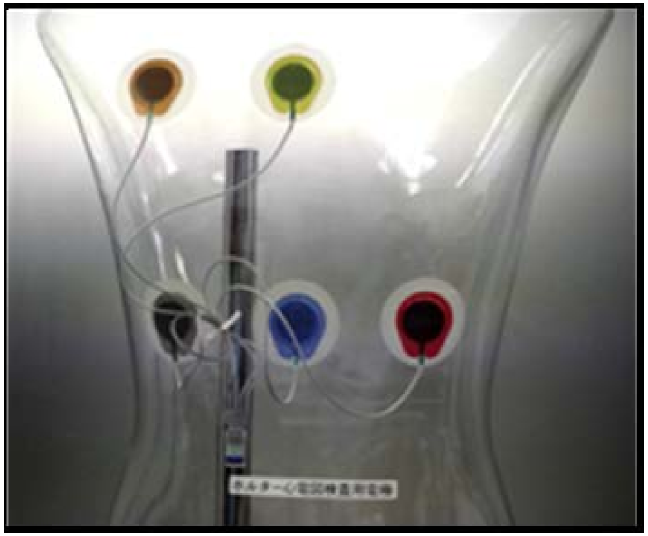
[JP60-193442,JP3513607]

★Polymerizability,Low toxicity,Adhesion

- NaSS
- Water soluble comonomer
- Divinyl monomer
- Additives
- Water

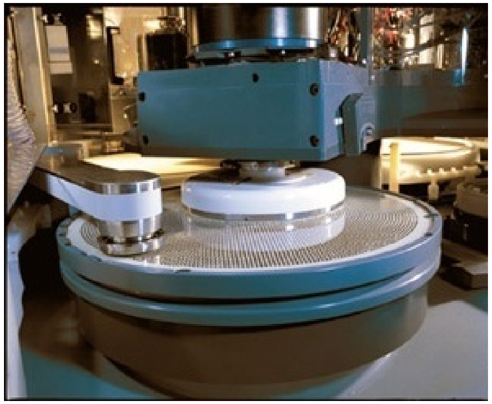
Radical polymerization





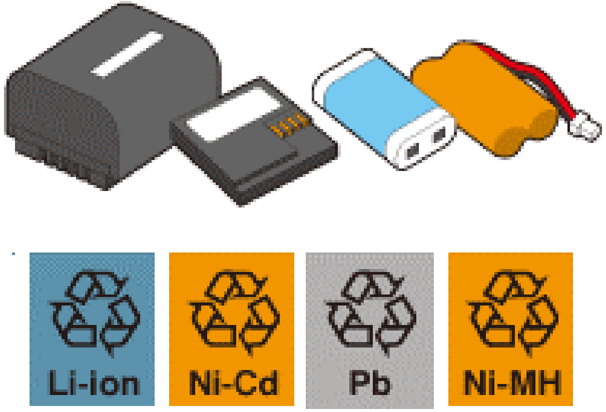
Gelatinous electric conductive material

Electronics



CMP

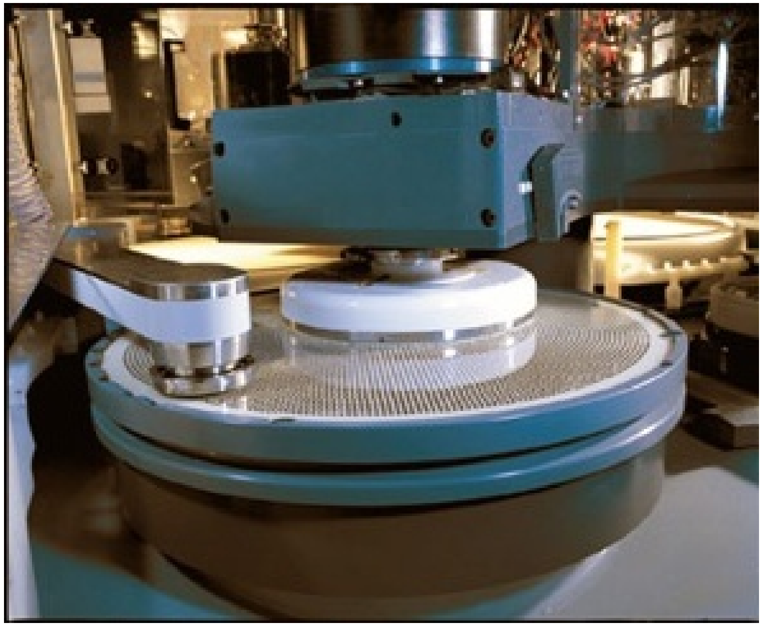
Conductive Polymer



Battery

Plating

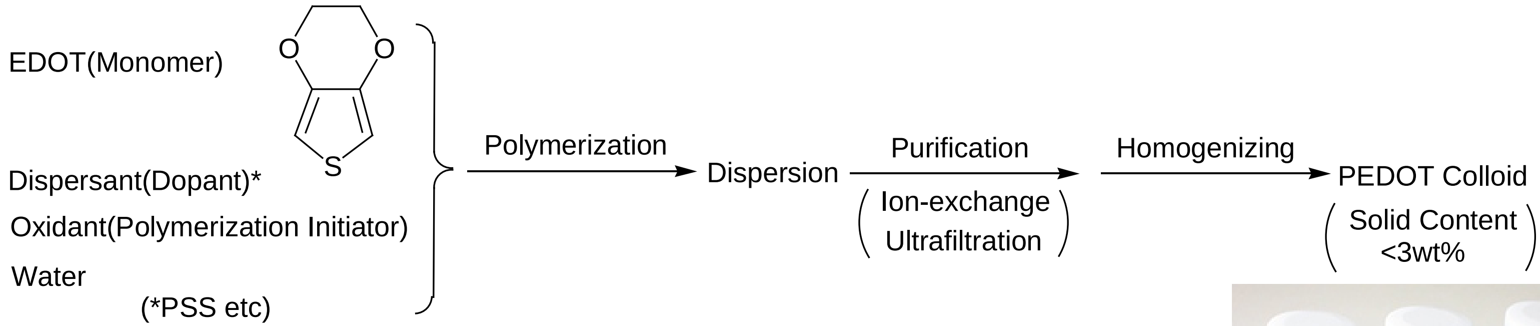
CMP Slurry and Washing Agent

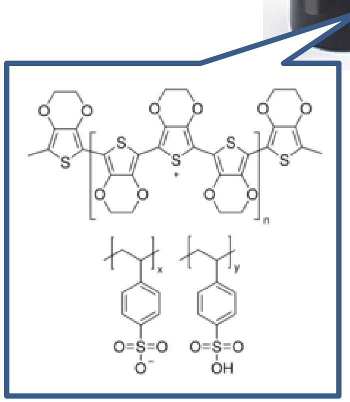


★Poly-NaSS acts as a dispersant for dust and abrasive grain.
★Poly-NaSS prevents scratch and excess abrasion of substrate by adsorption.
★Poly-NaSS is easily removed by washing.
★Poly-NaSS is not foamable.

PEDOT/PSS Colloid

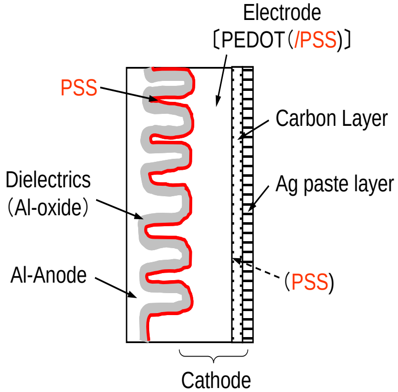
★Strong acid, Rigid chain, Dispersion

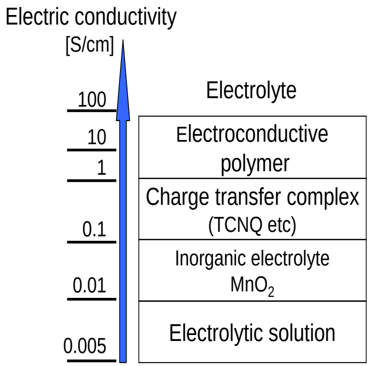




<Example use of Colloid(potential)>

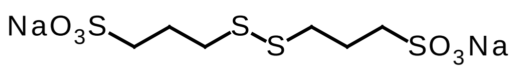
- Transparent Conductive Film
- Aluminum Solid Electrolytic Capacitor



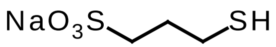


Plating

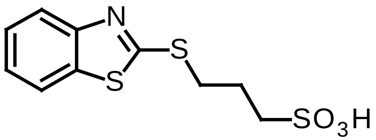
Conventional Sulfur Compounds

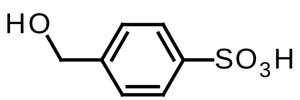


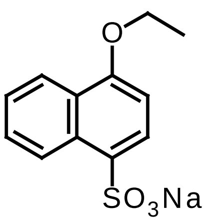
SPS

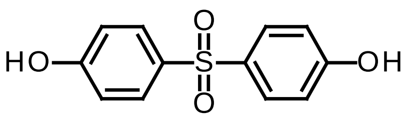


MPS

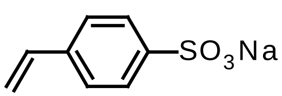




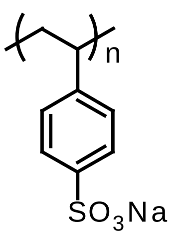




NaSS and poly-NaSS has been adopted.



NaSS



PS-1