SNF

National Nanotechnology Coordinated Infrastructure

Post Etch Wafer Clean

Usha Raghuram

Stanford Nanofabrication Facility

Stanford University

SNF

National Nanotechnology Coordinated Infrastructure

Cleans - Overview

Cleans in Fab Processes – Purpose:

- Resist removal
- Surface preparation
- Remove particles
- Remove organics
- Remove metals

Cleans Can be categorized into -

- Pre-deposition / oxidation clean
- Post etch clean

Factors in choosing a clean process/ chemistry –

- Type of residue to be removed
- Type of surface exposed to during cleans
- Ability to remove residues and contaminants without attacking the device materials

Clean Mechanism

- Chelation/ complex formation
- Solubilization and dissolution
- Undercut and lift off

Wet Cleans - Overview

Pre-Deposition/ Oxidation Cleans (for substrates prior to metal deposition)

- Piranha Clean - Sulfuric acid/ H_2O_2 (9:1) , 120 - 150°C -Organics and residue removal
- SC1 Clean – DI water/NH4O4/H_2O_2 (5:1:1), 50 - 80°C - Organics and particle removal
- SC2 Clean – DI water/HCl/H_2O_2 (5:1:1), 50-80°C – Metallic contamination removal
- 50:1 HF dip – Native oxide removal (50:1HF can be used either in between SC1 and SC2 or after SC1 & SC2)

Post Etch (on substrates without metal) Cleans – Typically after plasma resist strip (dry strip)

- Piranha clean (with or without plasma strip) – resist strip and etch residue removal
- 50:1 HF dip – For sidewall passivation removal after Si etch

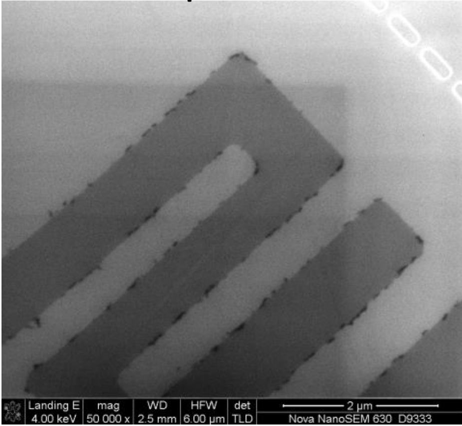
Post Etch (on substrates with exposed or buried metals and other acid sensitive films) Cleans – Typically after dry strip

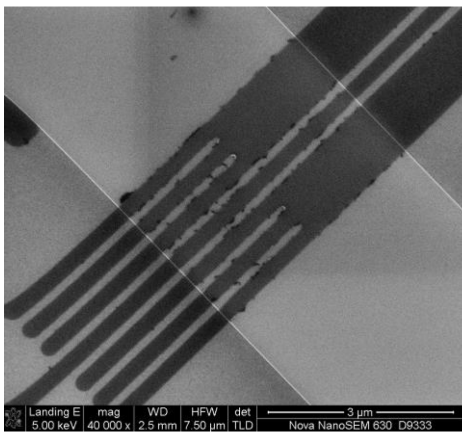
- Chemical mix - solvents semi-aqueous chemistries or dilute acids, buffered etchants etc. – Formulations w/ Surfactants, chelating agents ..

Etch Residues & Post Etch Cleans

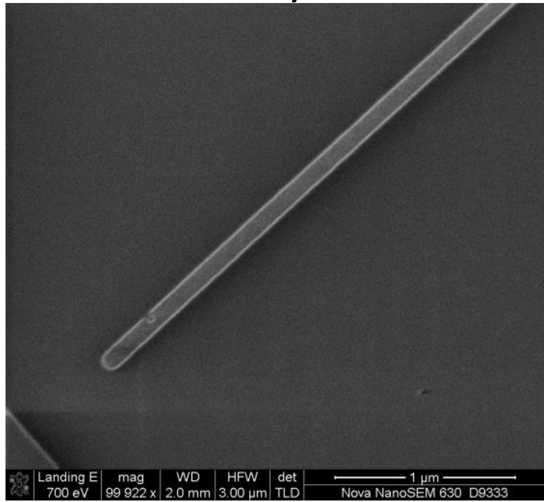
Internal Data

Etch Residues – Black Spots

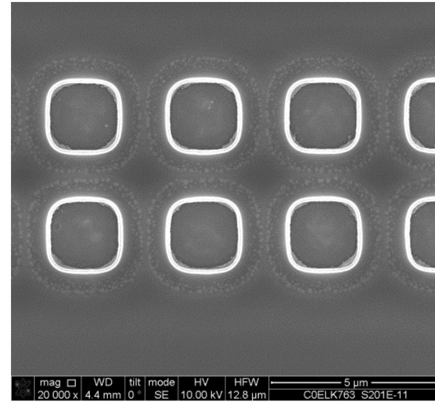




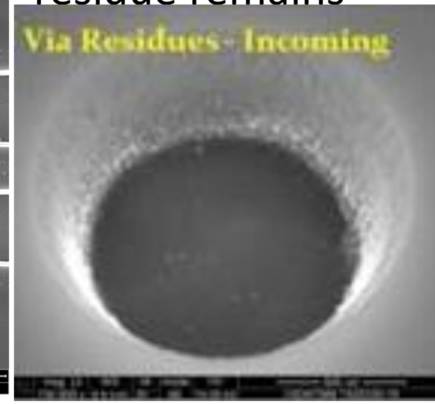
Etch residues Removed by Clean



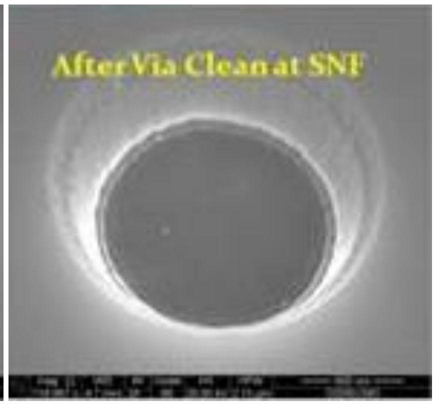
Etch Residues – Post Plasma Strip



Post Plasma Strip & wet Clean – Still some residue remains



Clean Vias - 2nd EKC265 Clean at SNF



From Semiconductor FabTech 31st Edition, P. 92 – Post Etch Residue Removal Challenges.. By Mertens et al. IMEC

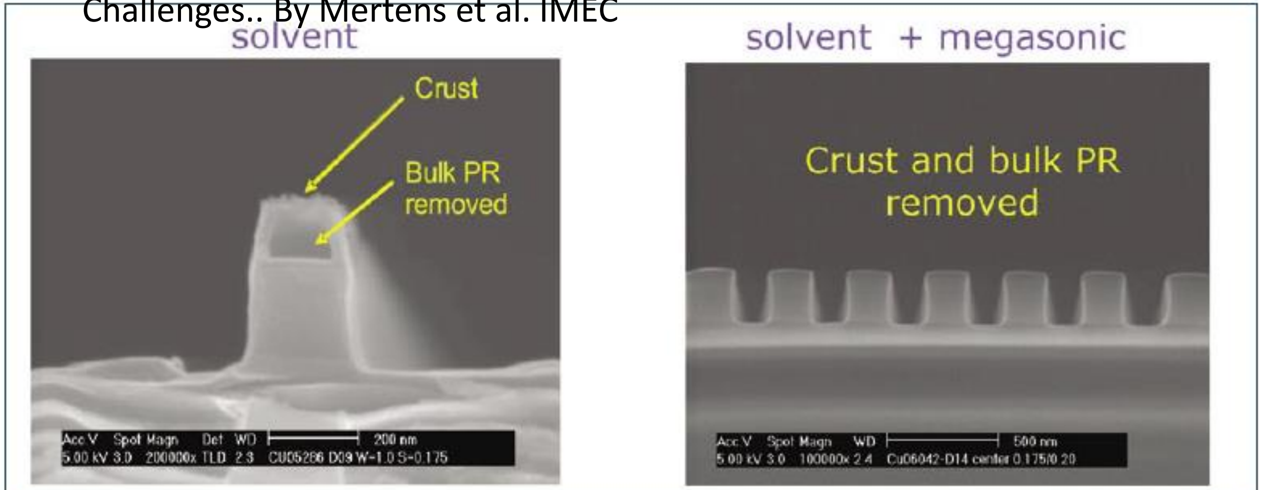
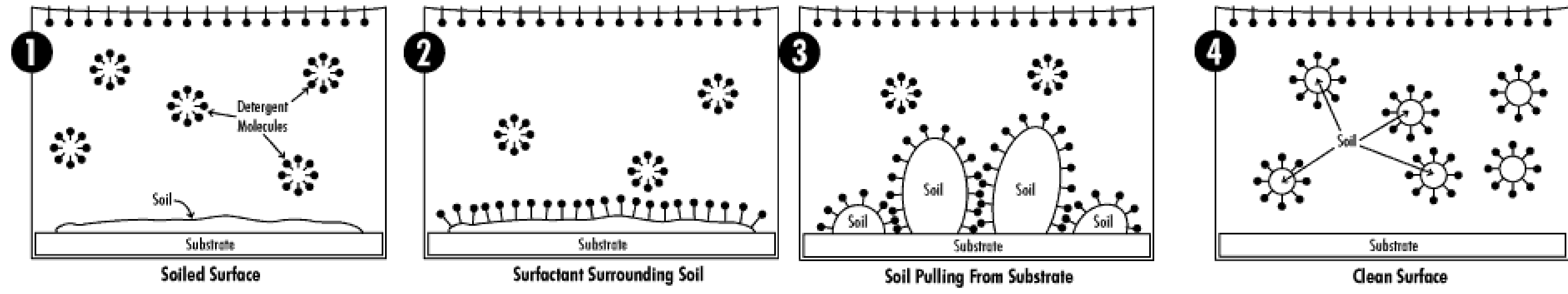


Figure 8. (left) With appropriate solvents the bulk PR can be dissolved leaving the crust only. (right) Solvent with megasonic agitation leads to complete strip without prior ashing [26].

SNF

National Nanotechnology Coordinated Infrastructure

Surfactants

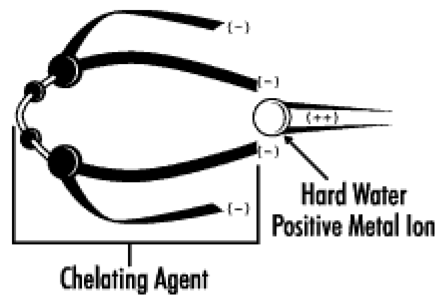


- From - https://www.essind.com/chemistry-of-cleaning/
- A surfactant is the most important part of any cleaning agent. The word surfactant is short for "Surface Active Agent."
- In general, surfactants are chemicals that, when dissolved in water or another solvent, orient themselves at the interface (boundary) between the liquid and a solid (the dirt we are removing), and modify the properties of the interface.
- How does a surfactant work? All have a common molecular similarity. One end of the molecule has a long nonpolar chain that is attracted to oil, grease, and dirt (the hydrophobe). Another part of the molecule is attracted to water (the hydrophile).
- The surfactant lines up at the interface as diagrammed below. The hydrophobic end of the molecule gets away from the water and the hydrophilic end stays next to the water.
- When dirt or grease is present (hydrophobic in nature) the surfactants surround it until it is dislodged from the boundary. Notice in diagram 4 that the dirt molecules are actually suspended in solution.

SNF

National Nanotechnology Coordinated Infrastructure

Chelating Agents



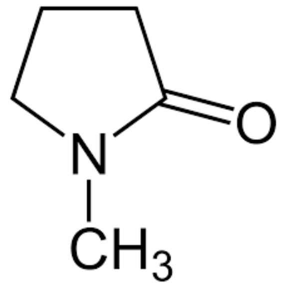
- From: https://www.essind.com/chemistry-of-cleaning/
- Soil removal is a complex process that is much more involved than just adding soap or surfactant to water. One of the major concerns we have in dealing with cleaning compounds is water hardness.
- Water is made "hard" by the presence of calcium, magnesium, iron and manganese metal ions.
- These metal ions interfere with the cleaning ability of detergents. The metal ions act like dirt and "use up" the surfactants, making them unavailable to act on the surface we want to clean.
- A chelating agent (pronounced kee-lat-ing from the Greek word "claw") combines itself with these disruptive metal ions in the water.
- The metal ions are surrounded by the claw-like chelating agent which alters the electronic charge of the metal ions from positive to negative (see diagram below.)
- This makes it impossible for the metal ions to be precipitated with the surfactants.
- Thus, chelated metal ions remain tied up in solution in a harmless state where they will not use up all of the surfactants.
- The surfactants are then able to do their job of actually removing soil and cleaning the surface.

Some Post Metal Etch Clean Chemistries

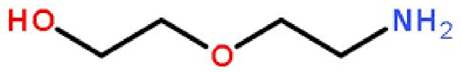
Post metal clean chemistries	Product Name		PRX-127	PRS-1000	SRS-100	Aleg-380	PRS-3000	EKC-265	SVC-14
	Manufacturer		Baker	Baker/ Avantor		Baker/ Avantor		DuPont	Dow/ Shipley
	Recommended Operating Temp		60-75 C	60-85 C	60-80 C	75-85 C		65-75 C	
CAS Number and Chemical Composition	872-50-4	NMP = N-Methyl-2-Pyrolidinone		35-55%	40-60%	40-60%	40-60%		
	141-43-5	Ethanolamine				20-40%			
	96-48-0	Butyrolactone							>40%
	929-06-6	2-(2-aminoethoxy) Ethanol						Yes	
	78-96-6	2-Propanol, 1-amino			5-15%		5-15%		
	7803-49-8	Hydroxylamine						Yes	
	10424-65-4	TMAH, Tetramethyl ammonium hydroxide pentahydrate	less than 4%						
	120-80-9	Catechol				2.5-10%		Yes	
	112-60-7	Tetraethylene glycol		1-10%					
	111-90-0	Diethylene glycol monoethyl ether		10-20%					
	34590-94-8	Dipropylene glycol monometheyl ether	less than 30%						
		Proprietary alcohol, TSRN600435129-5014				5-20%			
	126-33-0	Thiophene, tetrahydro 1,1 dioxide		25-45%	30-50%		30-50%		
	67-68-5	DMSO, Dimethyl Sulfoxide	less than 75%						<60%
	77-79-2	Sulfolene							

Chemicals Used in Cleans

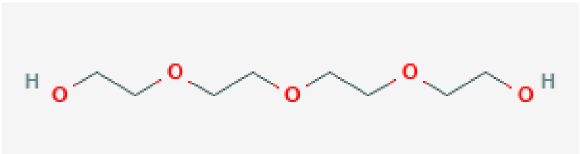
NMP



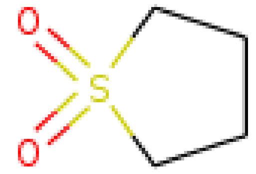
2-(2-aminoethoxy) Ethanol



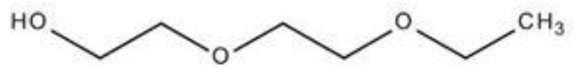
Tetraethylene glycol



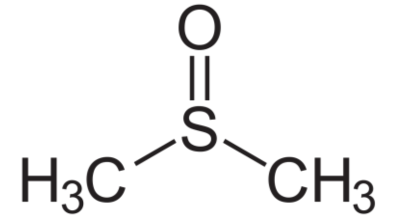
Thiophene, tetrahydro-1,1-dioxide



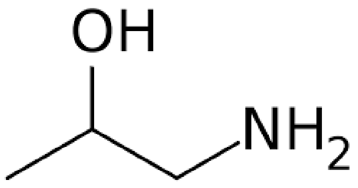
Diethylene glycol monoethyl ether



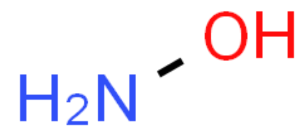
DMSO, dimethyl sulfoxide



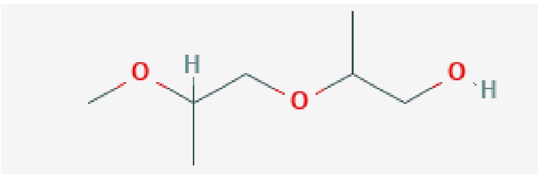
1-amino-2-propanol



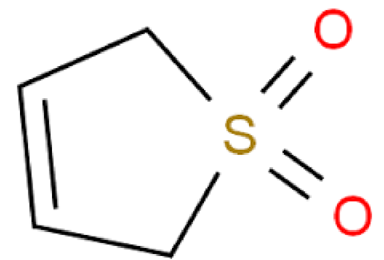
Hydroxyl amine



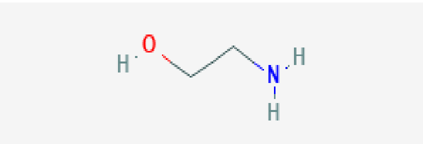
Dipropylene glycol monomethyl ether



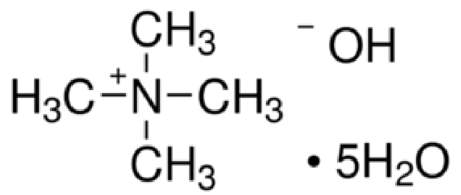
Sulfolene



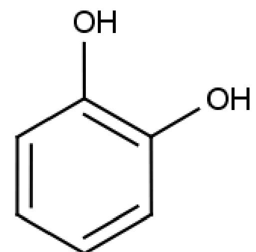
Ethanol amine



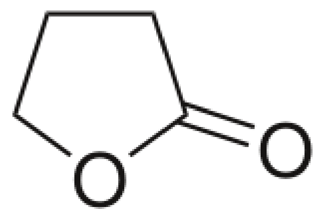
TMAH, pentahydro



Catechol

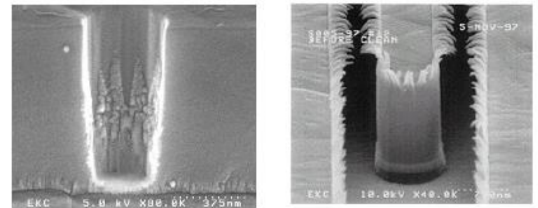


Butyrolactone

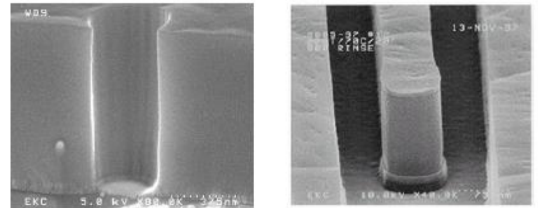


Etch Residues & Post Etch Cleans

Technical Notes from DuPont



Before Clean



After Clean with DuPont™ PlasmaSolv® post-etch residue remover

https://www.dupont.com/content/dam/dupont/amer/us/en/products/ei-transformation/documents/PlasmaSolve-PLS.pdf
https://www.dupont.com/content/dam/dupont/amer/us/en/products/ei-transformation/documents/EKC265.pdf

DuPont™ PlasmaSolv® post-etch residue removers are made with HDA® high-performance hydroxylamine-based cleaning technology. HDA® technology comprises aqueous organic mixtures formulated to effectively remove residues from substrate surfaces after via, poly and metal etch processes used in the microelectronics industry. Effective cleaning after dry etch process steps helps achieve high manufacturing yields and more reliable semiconductor devices for the higher performance and lower power consumption needed for cell phones, games, computers and other electronic devices. DuPont™ PlasmaSolv® products perform at low operating temperatures, well below the flashpoint of the chemistries, providing a safe chemical process as well as extending bath life.

DuPont™ PlasmaSolv® post-etch residue removers include:

EKC220™
This product is similar to EKC265™, but utilizes hydroxylamine more efficiently as a result of product optimization. Originally developed to address Ti undercut with a cost effective formulation.

EKC245™
Specifically designed to clean post-etch residues generated during the volume production of high capacity DRAM devices. Applications include residue removal post HBr-polysilicon etch and post metal etch.

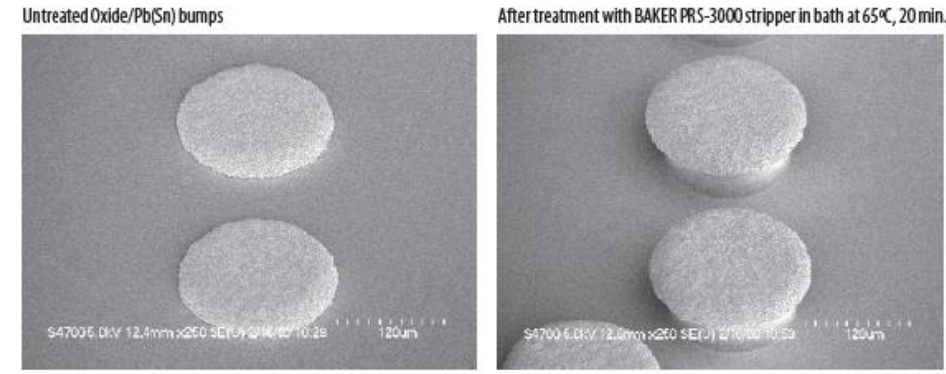
EKC265™
The initial product in the Plasmasolv® series formulated to remove photoresist residue generated after via and metal etch processes. Effective with or without oxygen ash processing.

EKC270™
Post-etch residue remover with improved Ti compatibility. Formulated to remove ashed photoresist residue, organic polymer, and organometallic etch residue while maintaining optimum metal stack integrity.

EKC270™-T
Post-etch residue remover with improved compatibility for Ti, W and Al on polysilicon, metal and high aspect ratio vias. Specifically formulated to meet the needs of customers who require a single chemistry for multiple post-etch residue cleaning applications due to its robust process window.

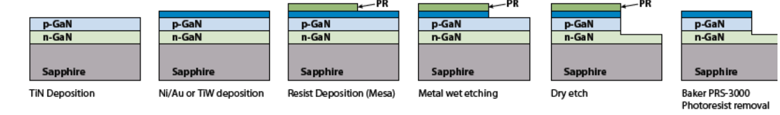
Technical Notes from Avantor on PRS-3000

https://www.avantorsciences.com/pages/en/resource-library



TECHNICAL INFORMATION

Metal Etch Rates (Å/min) at 85°C			Substrate Etch Rates (Å/min) at 85°C		
A1	Ti	W	GaAs	SiO_2	TEOS
<0.5	<0.4	0.3	<1	<1	<1



OPERATING GUIDELINES

See the full line of products which Avantor Performance Materials offers for legacy technology applications:

Photoresist Stripper/ Residue Remover	Product Number		Purpose	Application
	Bottles	Drum		
BAKER PRS™-1000	6383	6373	Positive Photoresist Stripper	Aluminum/Silicon Dioxide, Flip Chips, Bumps, Compound Semiconductors
BAKER PRS™-2000	6400	6410	Positive Photoresist Stripper	Flat Panel Display
BAKER PRS™-3000	6403	6413	Positive Photoresist Stripper	Aluminum/Silicon Dioxide, Flip Chips, Bumps, Compound Semiconductors
ALEG™-380	6475	6485	Residue Remover/Photoresist Stripper (Positive and Negative)	Aluminum/Silicon Dioxide, Flip Chips, Bumps, Compound Semiconductors
BAKER REZI™-38	6427	6437	Residue Remover	Aluminum/Silicon Dioxide, Copper Low-κ, Compound Semiconductors
BAKER REZI™-98	6508	6518	Residue Remover	Aluminum/Silicon Dioxide, Copper Low-κ, Compound Semiconductors
J.T.Baker® CLκ-820	6414	6424	Photoresist Remover	Copper Low-κ
J.T.Baker® CLκ-888	5108	5118	Residue Remover/Photoresist Stripper	Copper Low-κ
Experimental products	on request	on request	on request	on request

Post Metal Etch Cleans - Summary

- Post metal etch cleans are needed for removing metal containing sidewall residues and etch hardened photoresist
- Amine, glycol or sulfoxide-based solvents complex with the metallic residues and solubilize the residues
- Chelating agents are better at removing the residues from the surface
- Added surfactants prevent them from redepositing on the etched surface
- As the chemicals are week acids or bases, they do not attack metals
- Some chemical formulations will need an intermediate rinse in isopropanol prior to water rinse to prevent corrosion
- Dilute acids, buffered HF are also viable options for post etch residue removal.