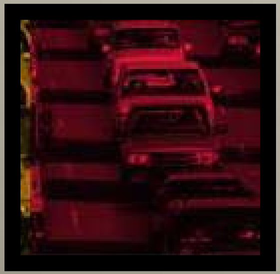
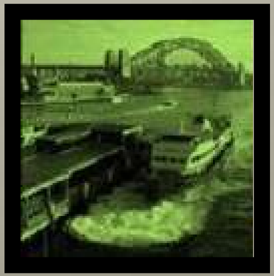
TRANSPORTATION RESEARCH BOARD
OF THE NATIONAL ACADEMIES

TRB Webinar:
Asphalt Emulsions: Chemistry, Manufacturing, and Applications

Today's Presenter and Moderator

Delmar Salomon, Pavement Preservation Systems LLC, dsalomon@mindspring.com

Alan James, AkzoNobel Surface Chemistry, alan.james@akzonobel.com

Introductory Remarks

Delmar Salomon
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Chair of TRB Committee AFK20
Characteristics of Bituminous Materials

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Asphalt Emulsion

Alan James
AkzoNobel Surface Chemistry

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Introduction to Asphalt Emulsion

- Asphalt
- The Chemistry of Emulsions
- The Chemistry of Emulsifiers
- The Setting process
- Emulsion Formulation
- Testing Emulsion
- Emulsion Applications

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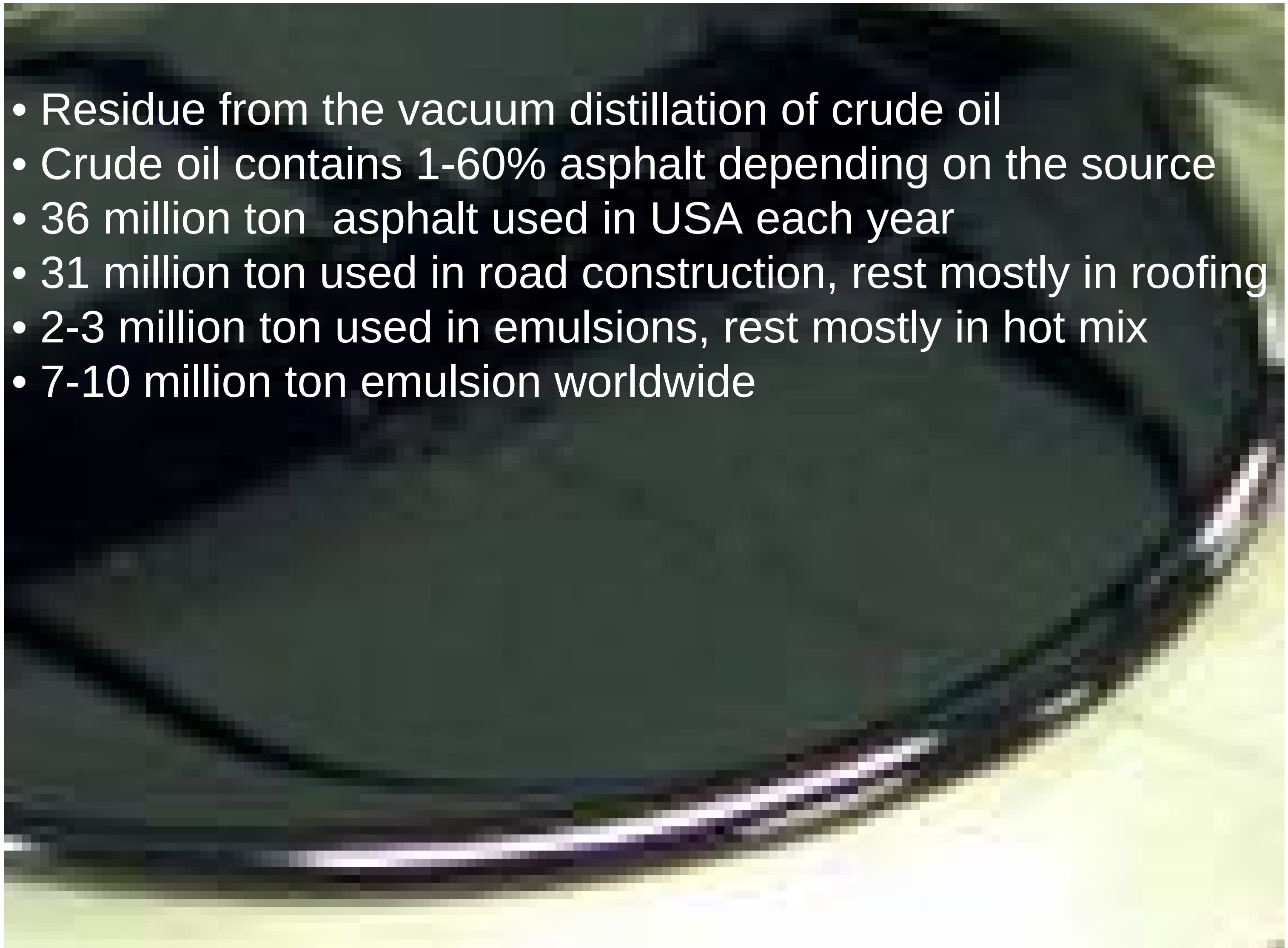
Asphalt



- Residue from the vacuum distillation of crude oil
- Crude oil contains 1-60% asphalt depending on the source
- 36 million ton asphalt used in USA each year
- 31 million ton used in road construction, rest mostly in roofing
- 2-3 million ton used in emulsions, rest mostly in hot mix
- 7-10 million ton emulsion worldwide

Asphalt

- Supplied in grades depending on its consistency/viscosity
- For emulsions viscosity is defined by tests like penetration and softening point
- The choice of asphalt depends on the end use.
- Most asphalt grades can be supplied in emulsion form.

Why Use Asphalt Emulsion

- Cold processes save energy
- Easier handling and storage
- Safe and environmentally friendly
- Low cost in place and on-site techniques
- Easily mixed with latex and cement
- Water dilutable
- Deferred Set

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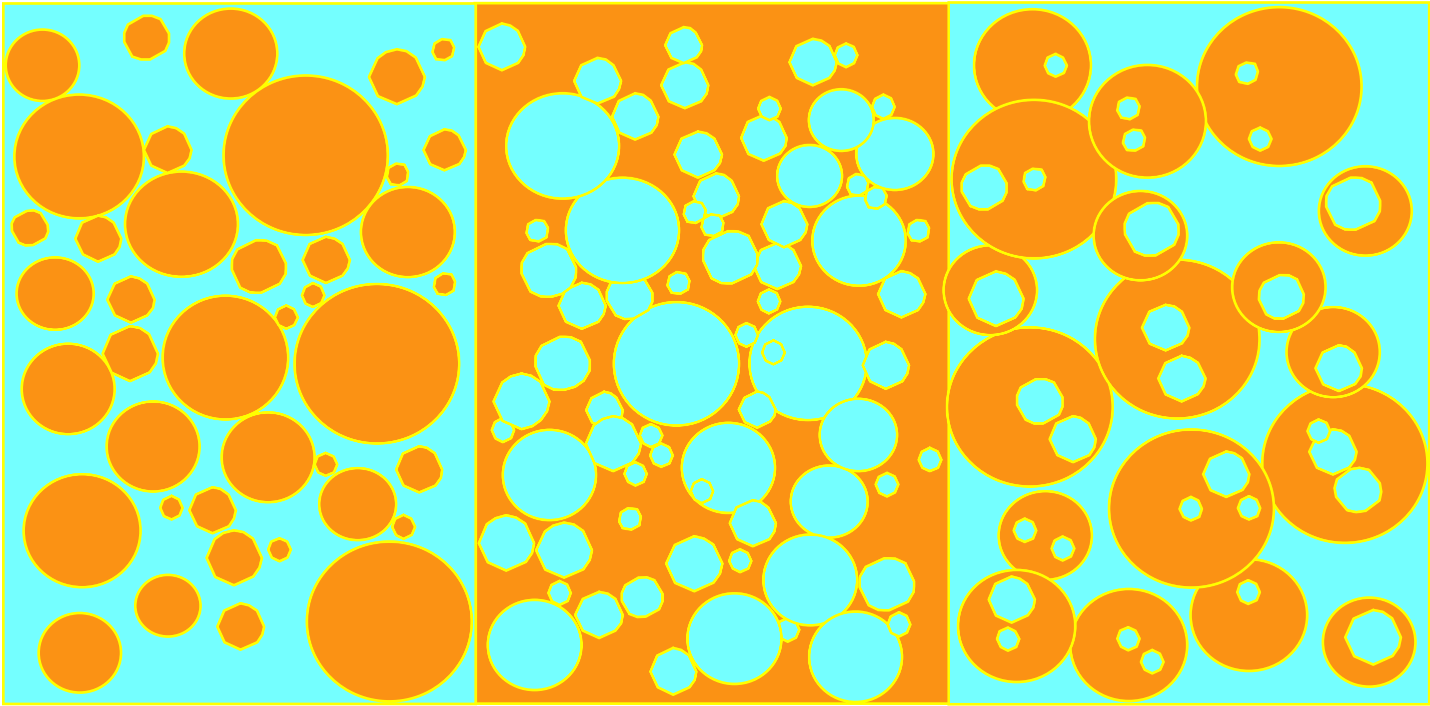
Emulsions around the Home

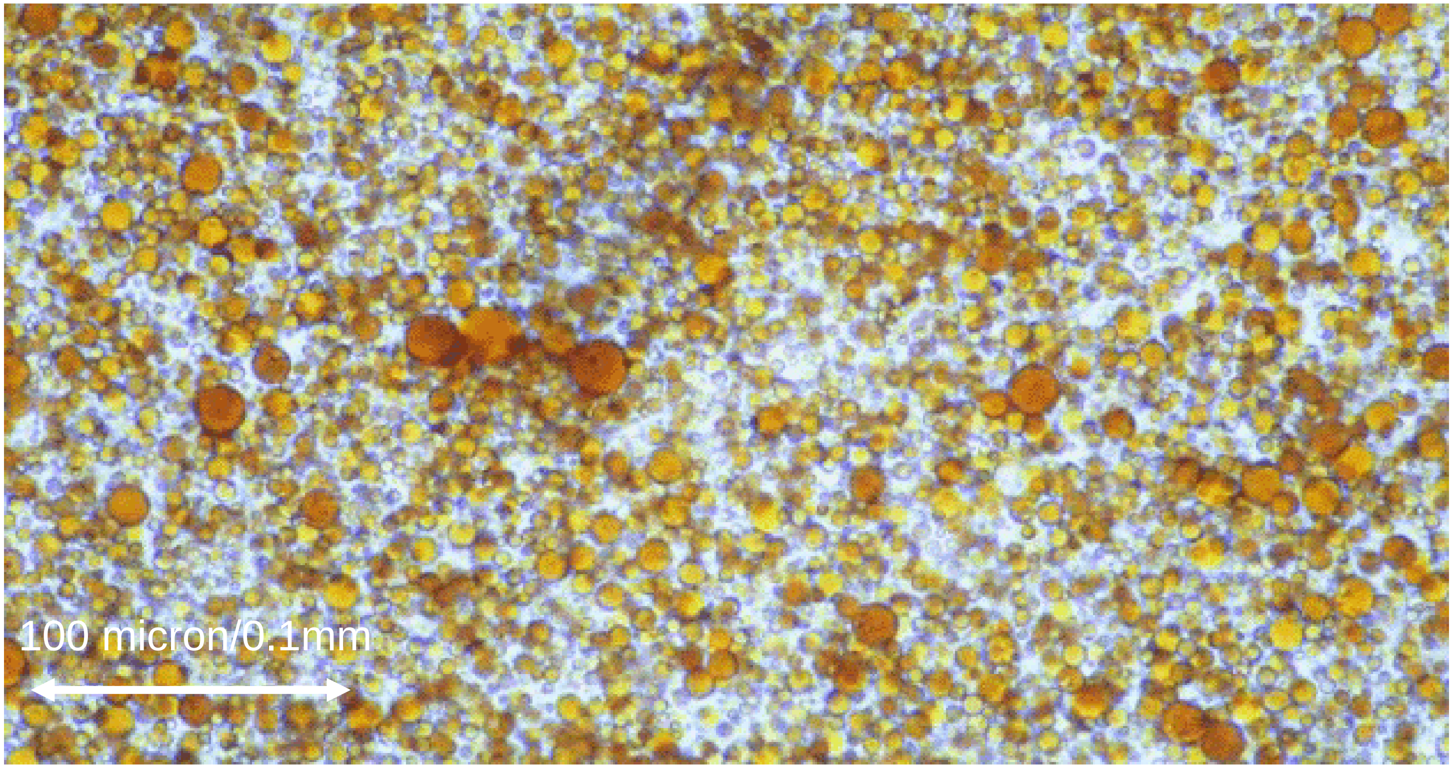
- Dispersion of one liquid in another (immiscible) liquid
- One of the liquids is usually water

Emulsion Types



O/W	W/O	W/O/W
oil-in-water emulsion	water-in-oil (invert emulsion)	multiple emulsion

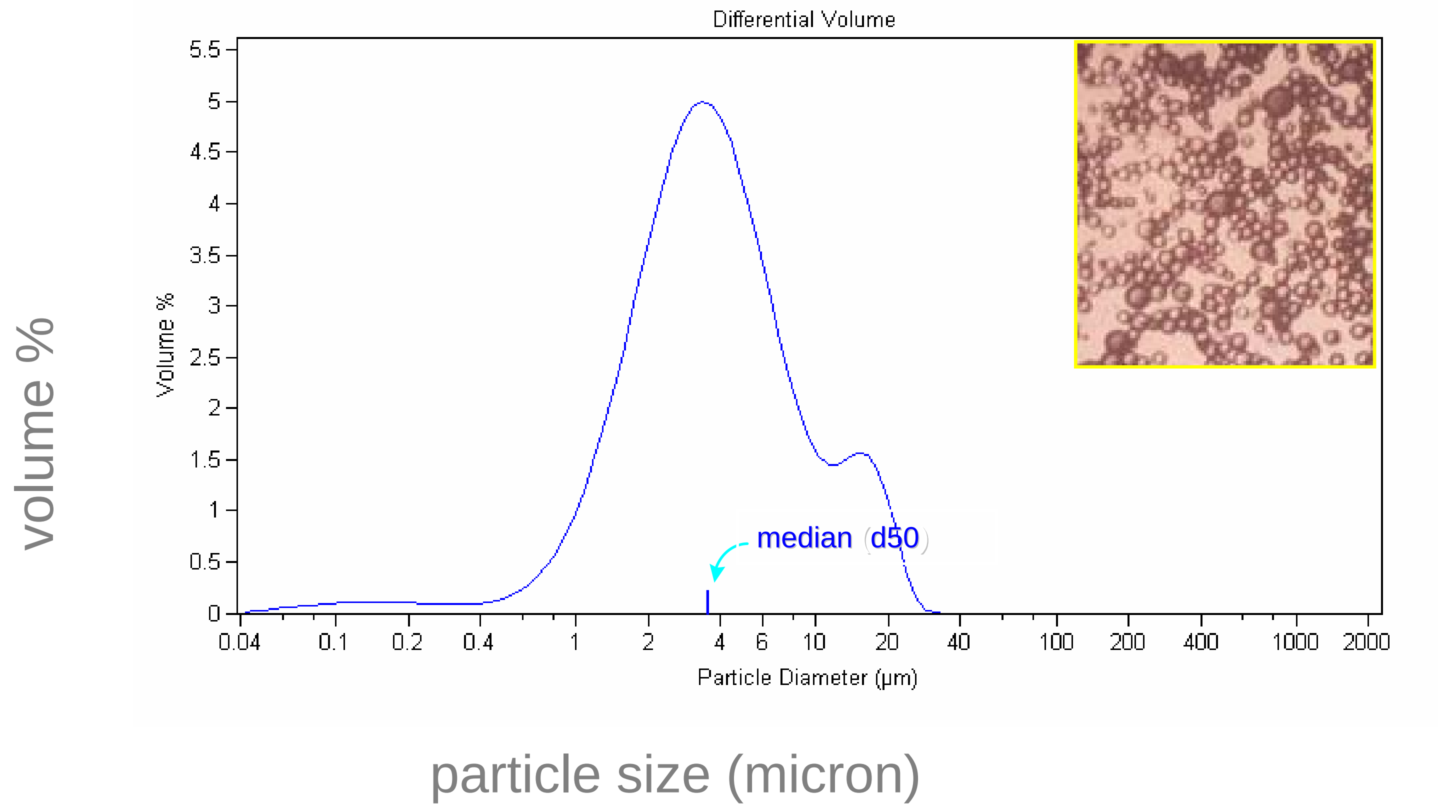
Photomicrograph of an Asphalt Emulsion



Source :BASF

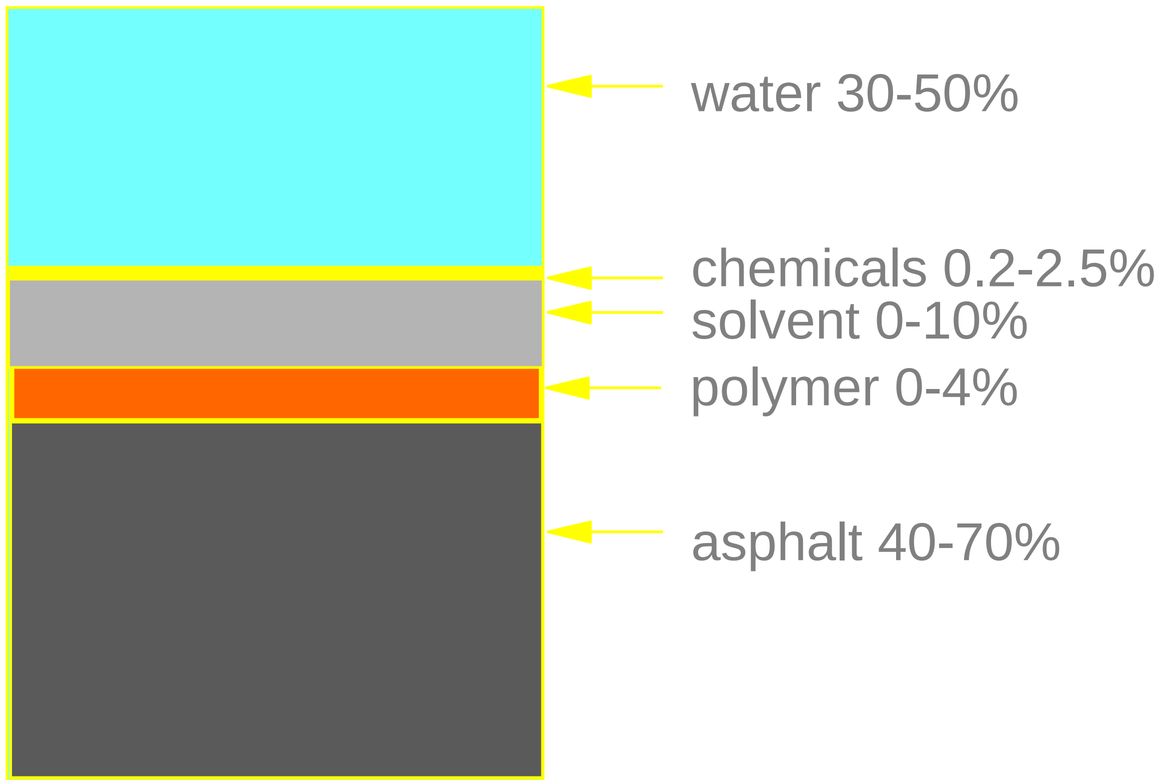
Droplets are spherical
Droplets are 1-20 micron in diameter
There is a distribution of particle sizes
Some asphalt droplets contain water droplets inside them

Size Distribution of Asphalt Emulsion Droplets



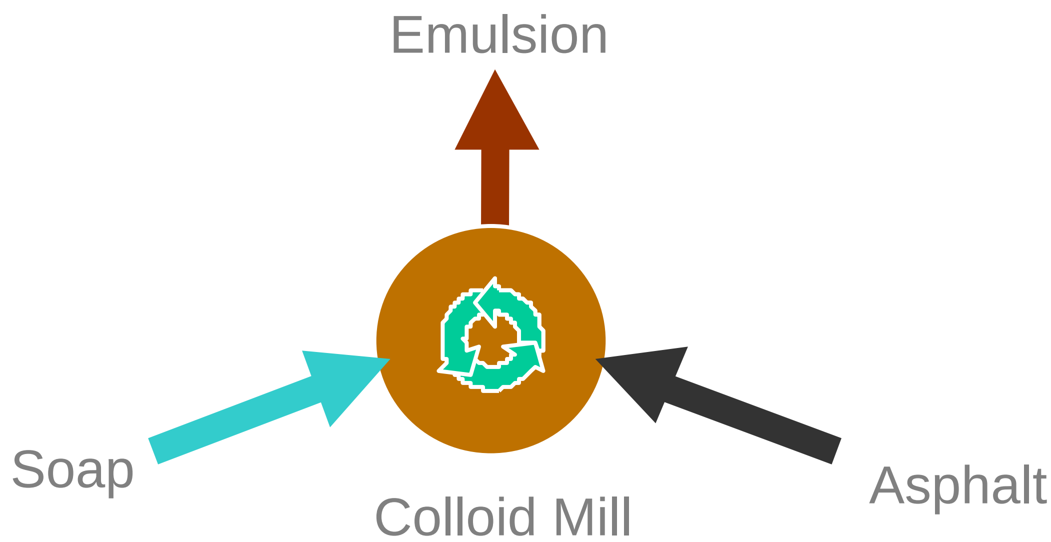
We can measure particle size distribution
The size depends on the emulsion recipe and manufacturing parameters.

Components of an Asphalt Emulsion



Production of Bitumen Emulsions

• Asphalt dispersed in a colloid mill into micron droplets in water



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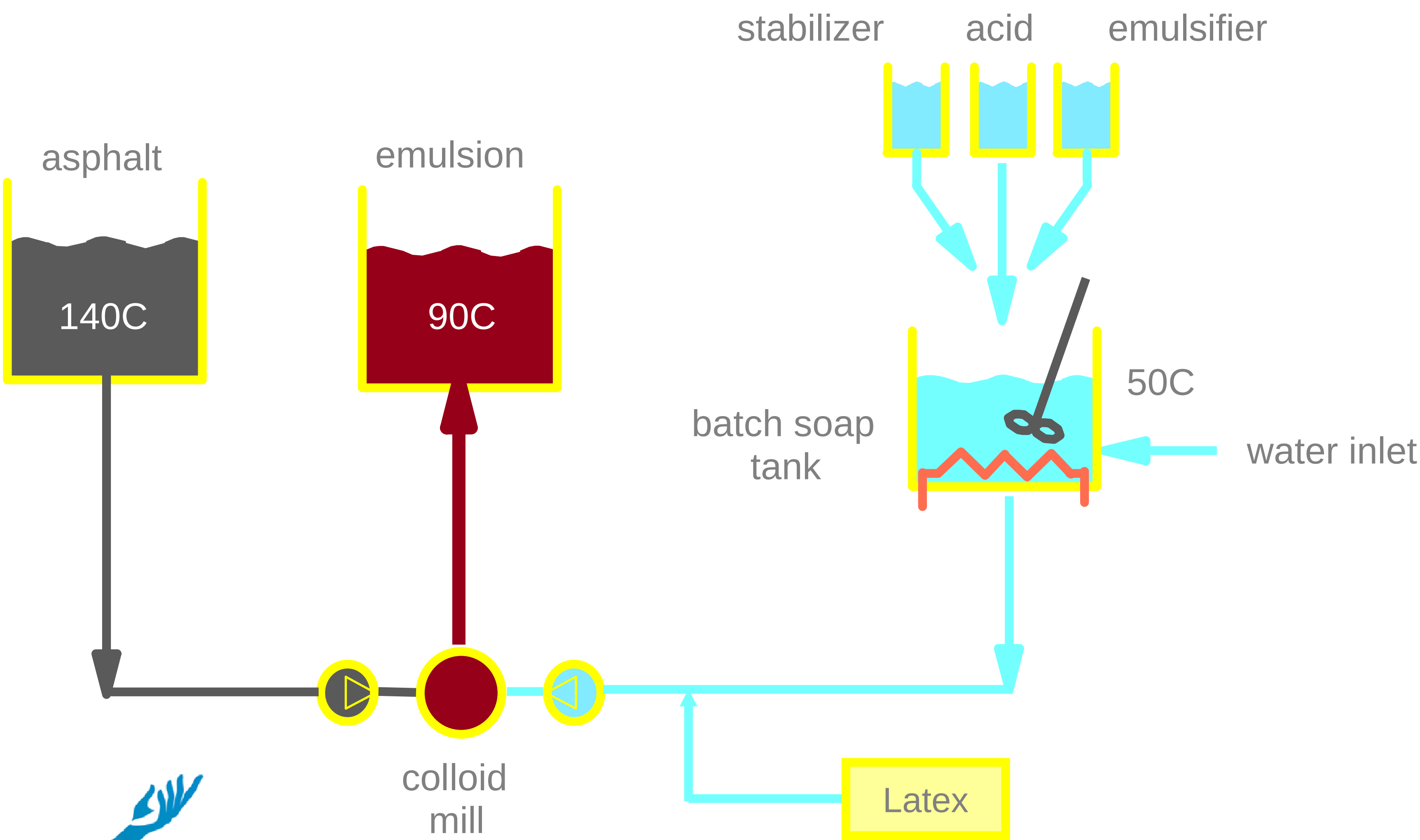
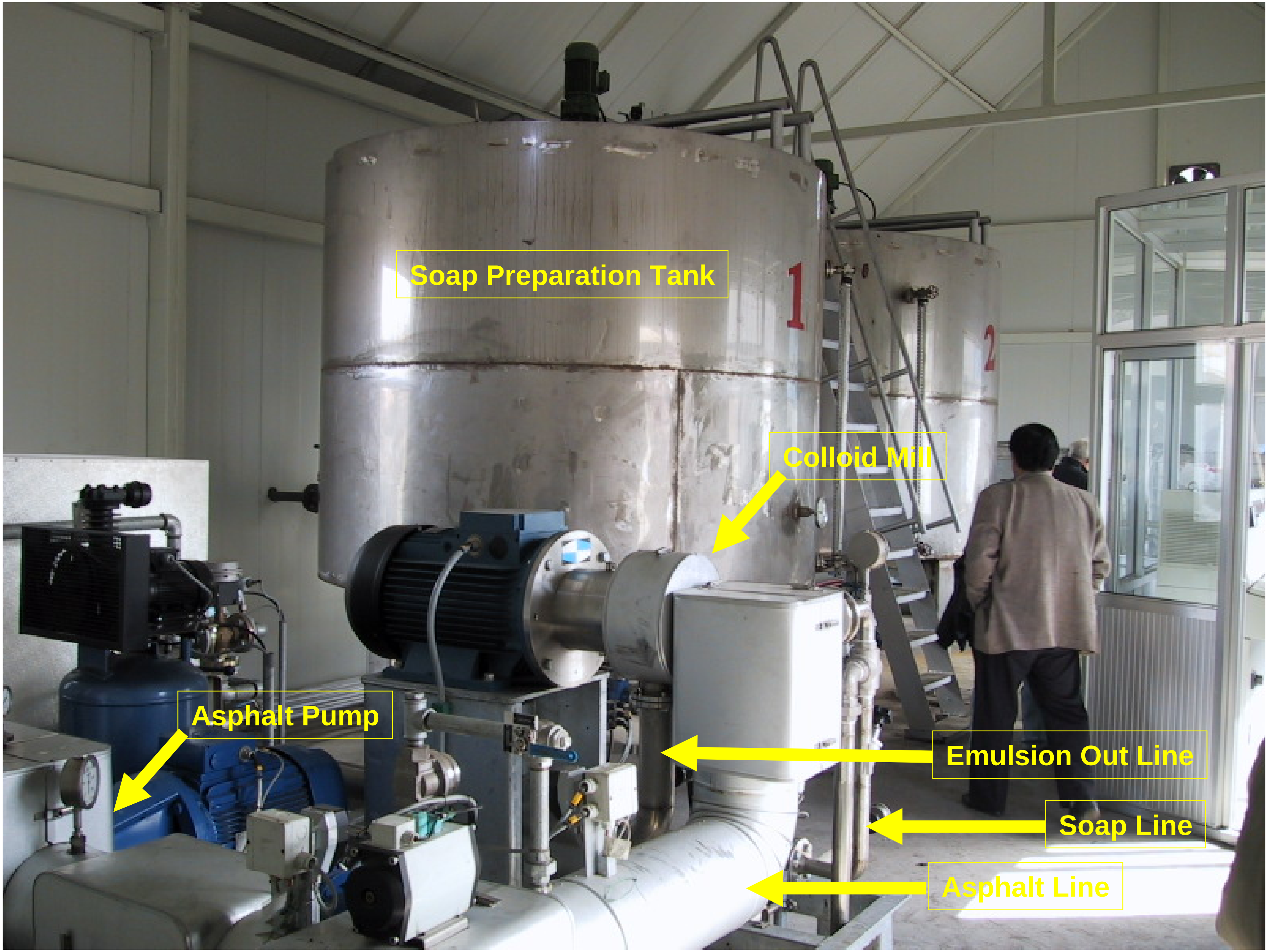
Inside the Colloid Mill

Schematic of Batch Emulsion Plant



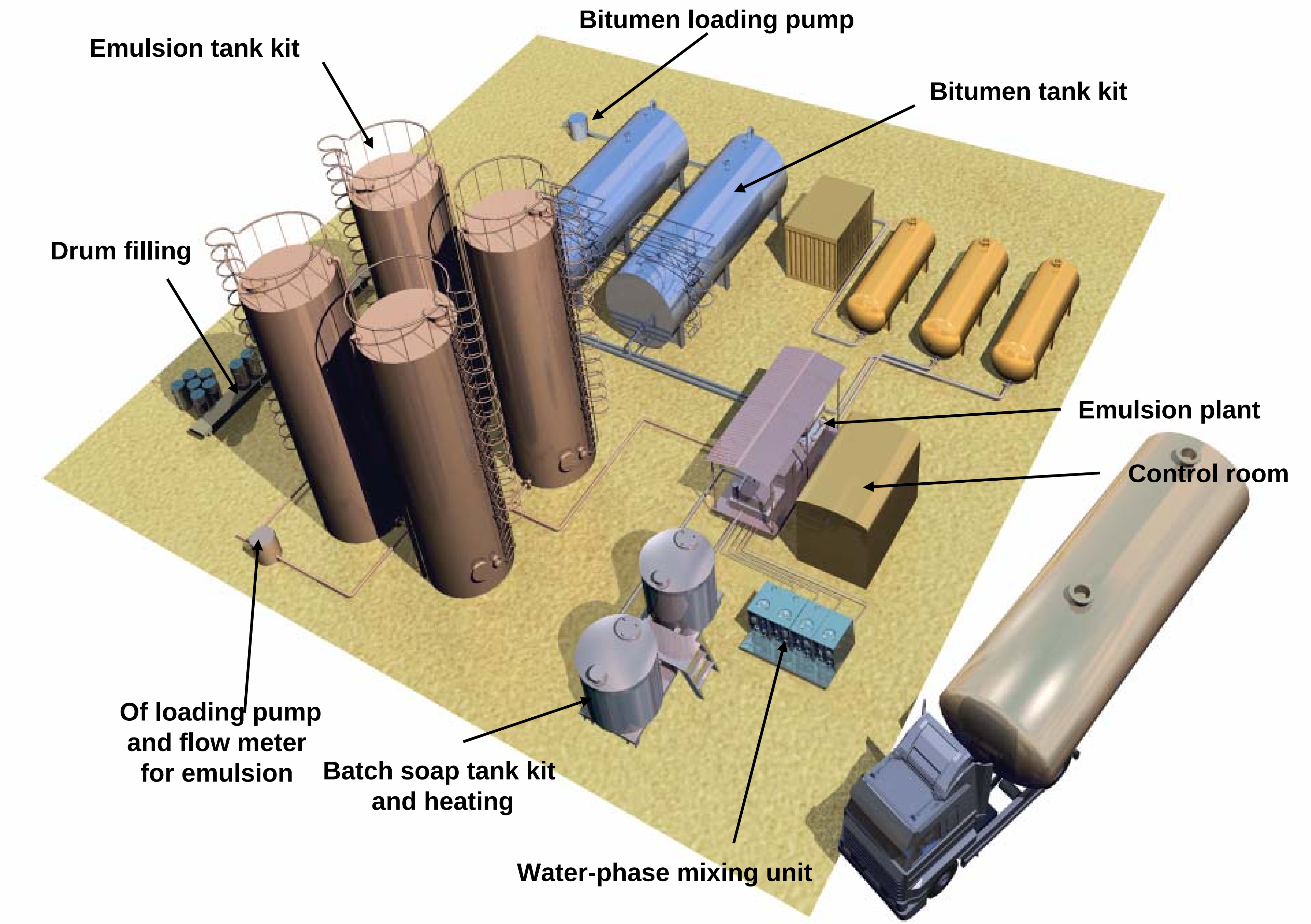


Soap Preparation Tank
Colloid Mill
Asphalt Pump
Emulsion Out Line
Soap Line
Asphalt Line

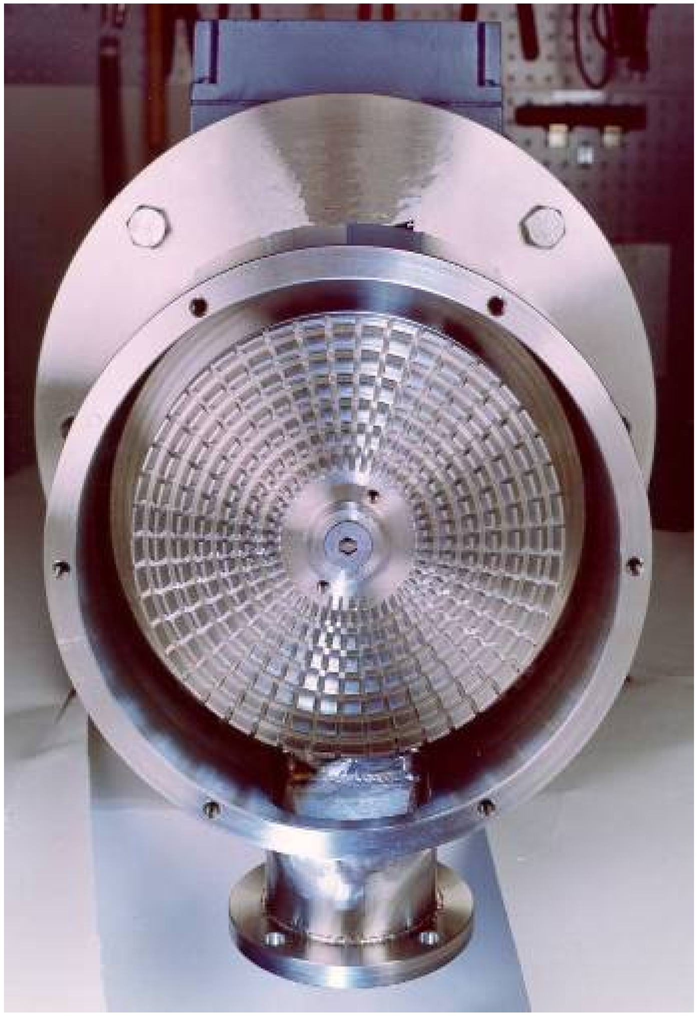

Inside the soap preparation tank


Inside the soap preparation tank


1
2
3
Emulsion Storage


Bitumen loading pump
Emulsion tank kit
Bitumen tank kit
Drum filling
Emulsion plant
Control room
Of loading pump
and flow meter
for emulsion
Batch soap tank kit
and heating
Water-phase mixing unit

Influences on Emulsion Quality



- Chemistry
- Asphalt & water flows
- Temperatures
- Speed of the mill
- Size of the mill

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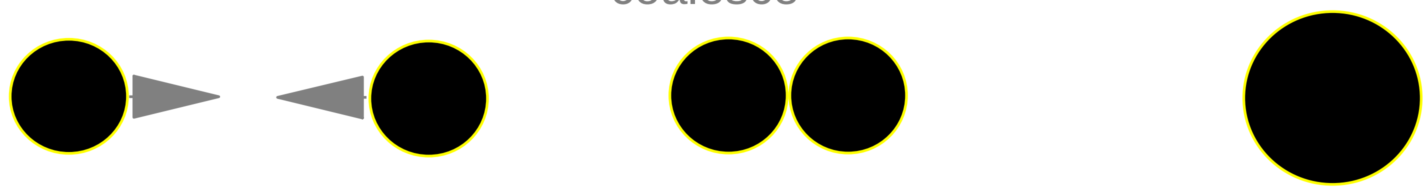
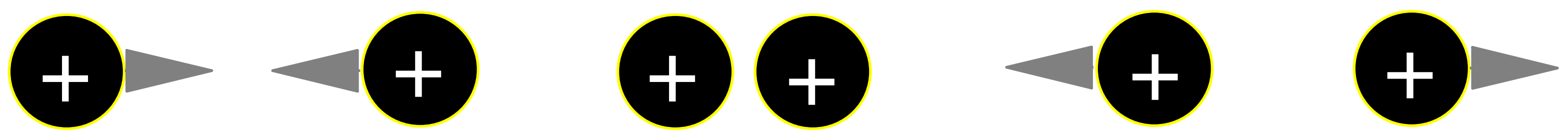
Stabilization of Asphalt Droplets

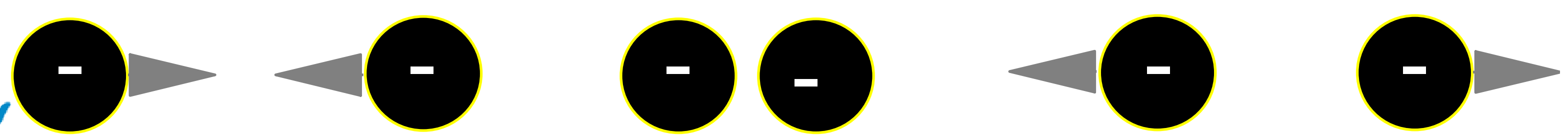
no charge- droplets can come into contact and coalesce



Cationic emulsion-electrostatic repulsion prevents close approach of drops



Anionic emulsion-electrostatic repulsion prevents close approach of drops



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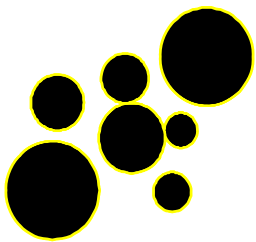
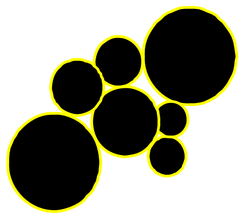
Breakdown of the Emulsion

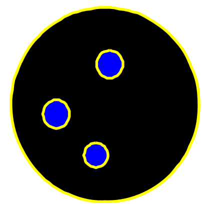
Flocculation and Coalescence



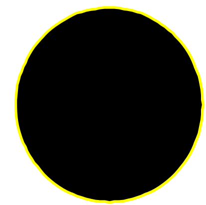
Emulsion Droplets
Charge on droplets prevents close approach



Flocculation
Close approach of droplets leads to adhesion between droplets. Water is squeezed out



Coalescence
Water drains between droplets and surfactant film breaks down, Droplets fuse, trapping some water



Coalescence
Trapped water diffuses out.

Setting

Curing

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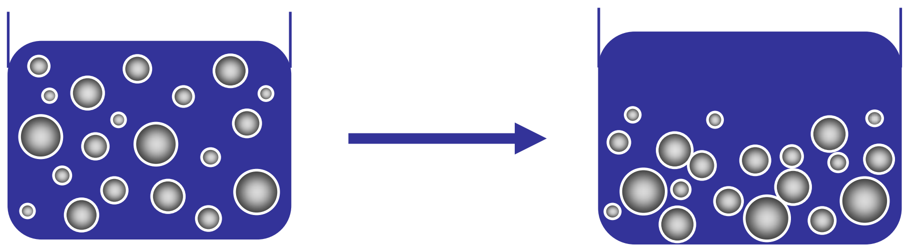
Breakdown of the Emulsion

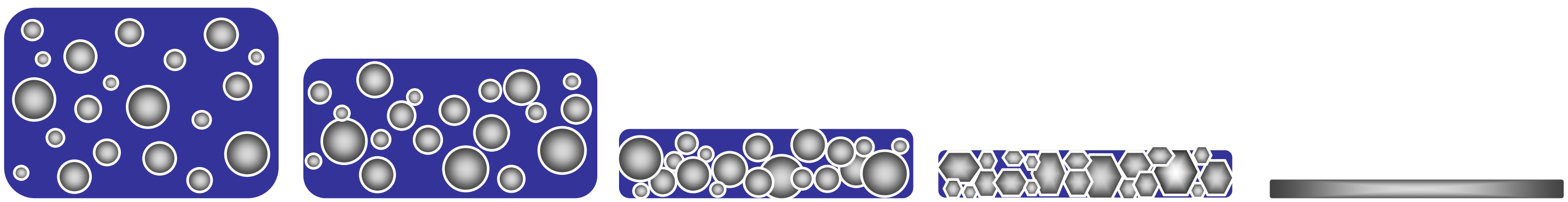
Settlement (Sedimentation)



- Asphalt is generally denser than water
- Sedimentation may lead to irreversible flocculation and/or coalescence

Breakdown of the Emulsion

Evaporation of Water



- Evaporation of water forces droplets together and eventual coalescence

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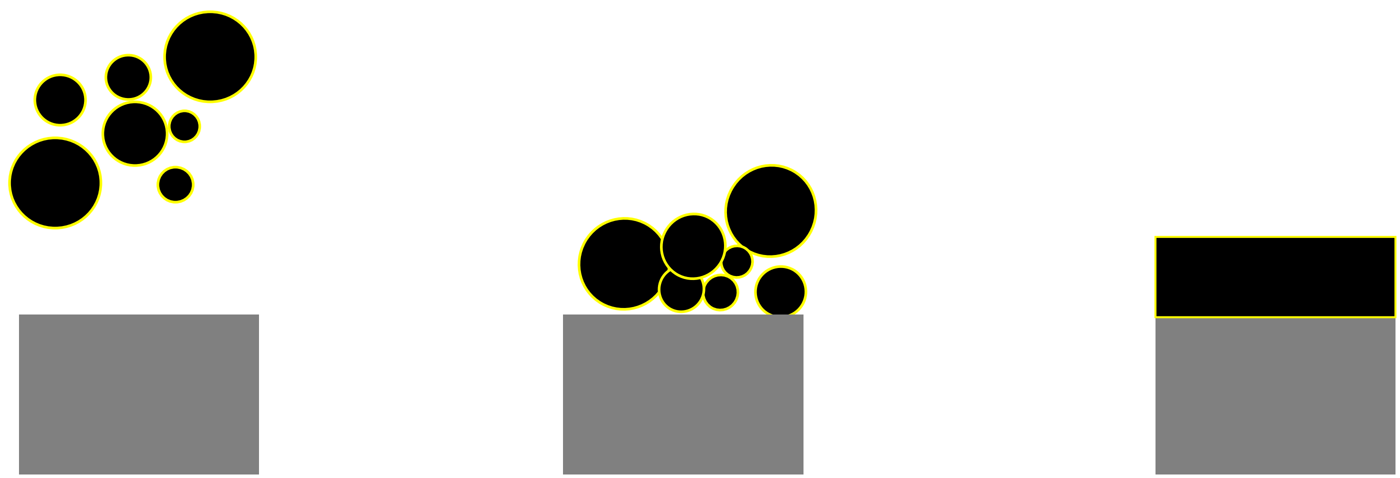
Breakdown of the Emulsion

Flocculation and Coalescence



- Flocculation and Coalescence in contact with Aggregate

Classification of Emulsion by Reactivity

rapid-setting:
reactive emulsion sets quickly even with unreactive aggregates

medium-setting:
medium reactive emulsion which can be mixed with open graded aggregates with low fines content

slow-setting:
low reactive emulsion which can be mixed with reactive aggregates with high fines content

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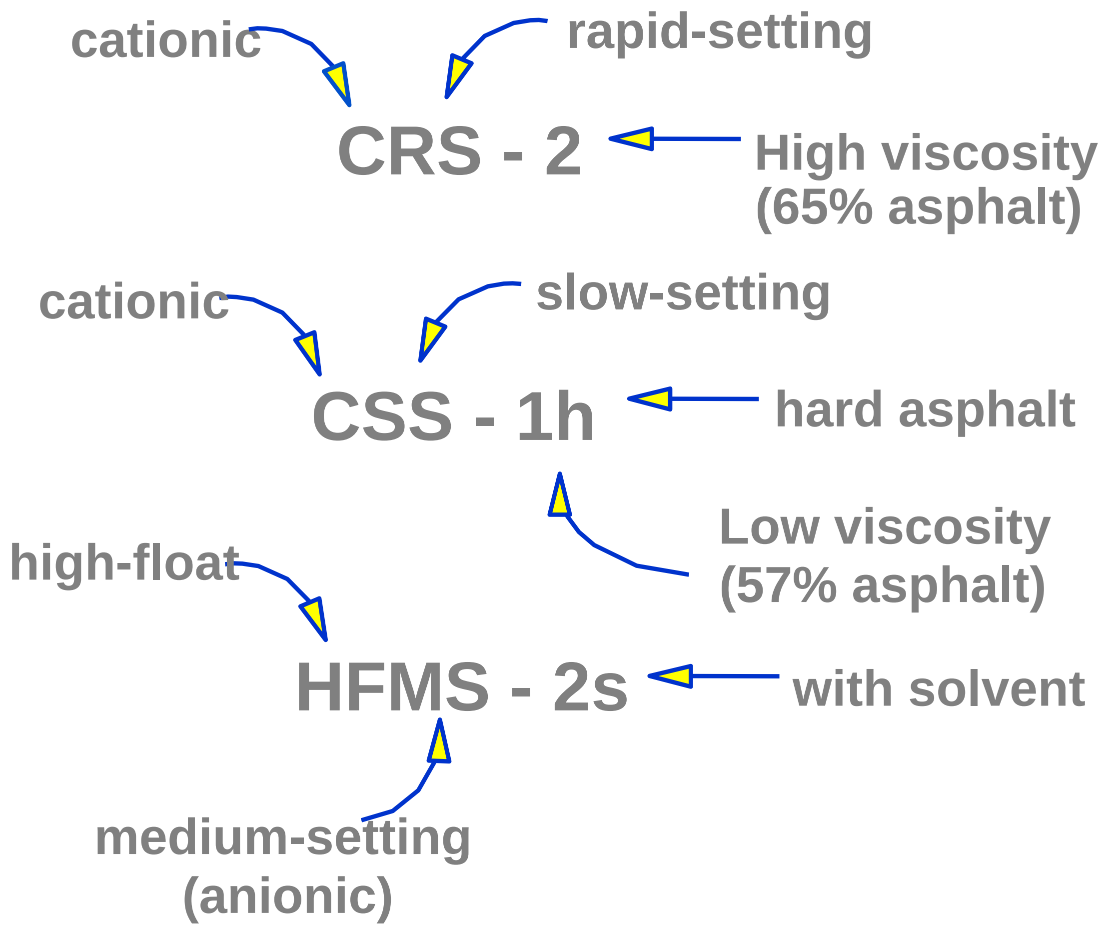
Naming of Emulsions



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Emulsions are classified according to Reactivity and Particle Charge

	+ve	-ve	
rapid-setting	CRS	RS	chip-seal
medium-setting	CMS	MS	open-graded mix
slow-setting	CSS	SS	dense-graded mix

The principle is to match the reactivity of the emulsion with the reactivity of the aggregate

Rapid - set emulsions are used with *unreactive,* low surface area aggregates

Slow – set emulsions are used with *reactive* high surface area aggregates

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Functions of the Emulsifier

- determines type of Emulsion formed. i.e. O/W or W/O
- reduces energy needed to emulsify asphalt
- determines charge on emulsion droplets
- stabilizes emulsion droplets as they are formed in the colloid mill
- stabilizes the droplets during storage of the emulsion
- provides the right setting behavior
- influences the physical properties of the emulsion
- influences properties of cured road material.

Typical Emulsifier Structures

Lipophilic/hydrophobic tail — hydrophilic head group — counterion

R(tallow) --------------------------------	**$N^{+}(CH_3)_3$**	**Cl^-**
R(tallow) --------------------------------	**$NH_2^{+}CH_2CH_2CH_2NH_3^{+}$**	**$2Cl^-$**
R(nonylphenyl) -----------------------	**O----$CH_2CH_2OCH_2CH_2O$---H**	**none**
R(tall oil)---------------------------------	**COO^-**	**Na^+**
R(lignin)----------------------------------	**SO_3^-**	**Na^+**

R= hydrocarbon or mostly hydrocarbon with 12-22 carbons
N= nitrogen, C=carbon, H= hydrogen, O= oxygen
S= sulfur, Cl= chlorine, Na = sodium

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Cationic emulsions tend to be acidic, anionic emulsions alkaline

$$RNHCH_2CH_2CH_2NH_2 + 2HCl = RNH_2^{+}CH_2CH_2CH_2NH_3^{+} \; 2Cl^{-}$$

insoluble neutral form + acid = soluble cationic 'soap'

$$RCOOH + NaOH = RCOO^{-} \; Na^{+}$$

insoluble neutral form + alkali = soluble anionic 'soap'

R= hydrocarbon or mostly hydrocarbon with 12-22 carbons
N= nitrogen, C=carbon, H= hydrogen, O= oxygen
S= sulfur, Cl= chlorine, Na = sodium

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Some charged emulsifiers do not need pH adjustment

$RN(CH_3)_3^{+}$ Cl^{-}

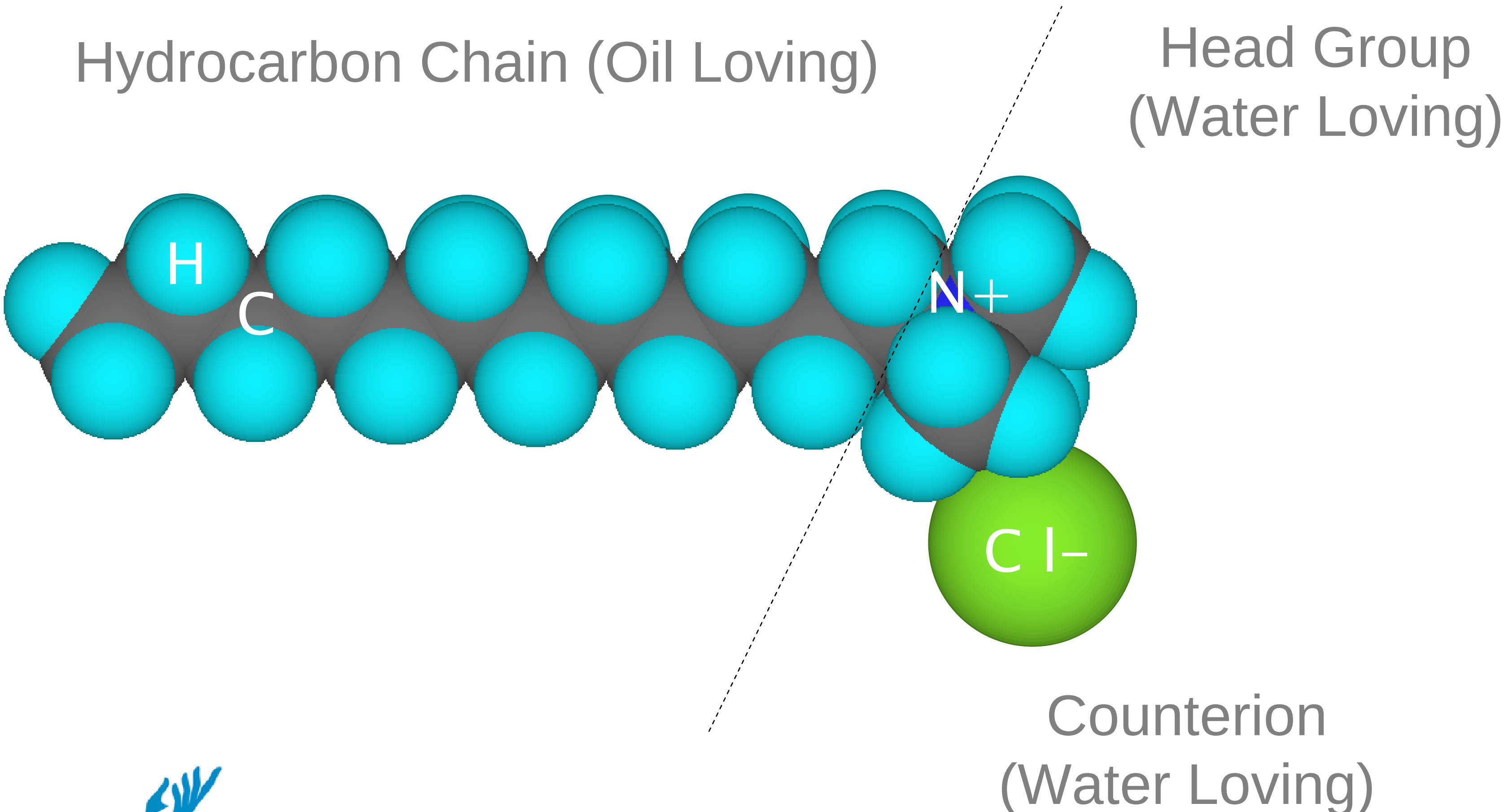
soluble quaternary amine

RSO_3^{-} Na^{+}

soluble olefin sulphonate

R= hydrocarbon or mostly hydrocarbon with 12-22 carbons
N= nitrogen, C=carbon, H= hydrogen, O= oxygen
S= sulfur, Cl= chlorine, Na = sodium

Cationic emulsifier



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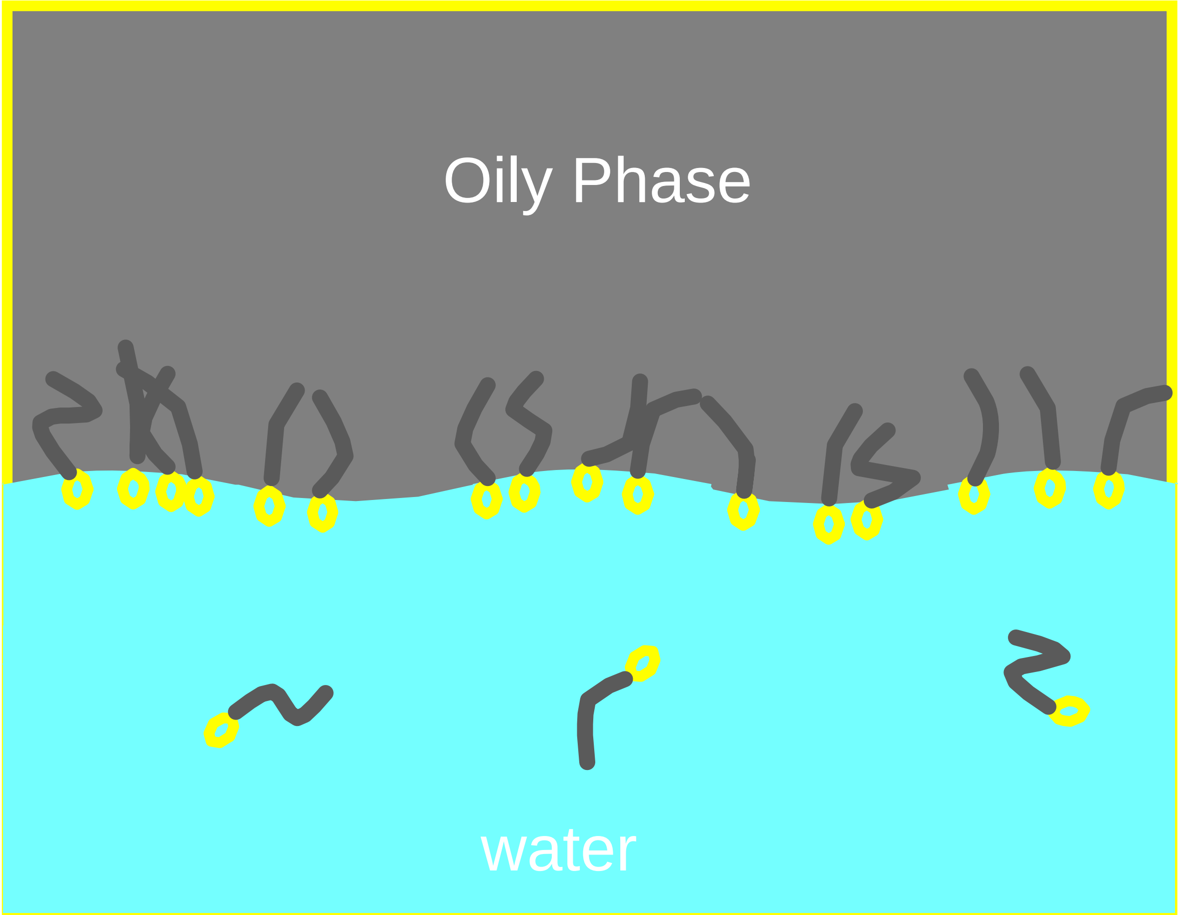
Emulsifier Molecules concentrate at the oil-water interface

"Tails" in the Oil and "Heads" in the Water



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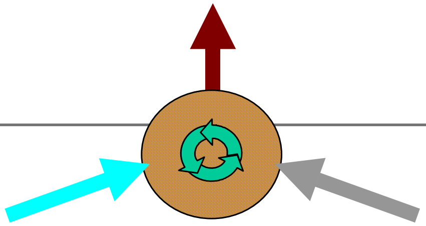
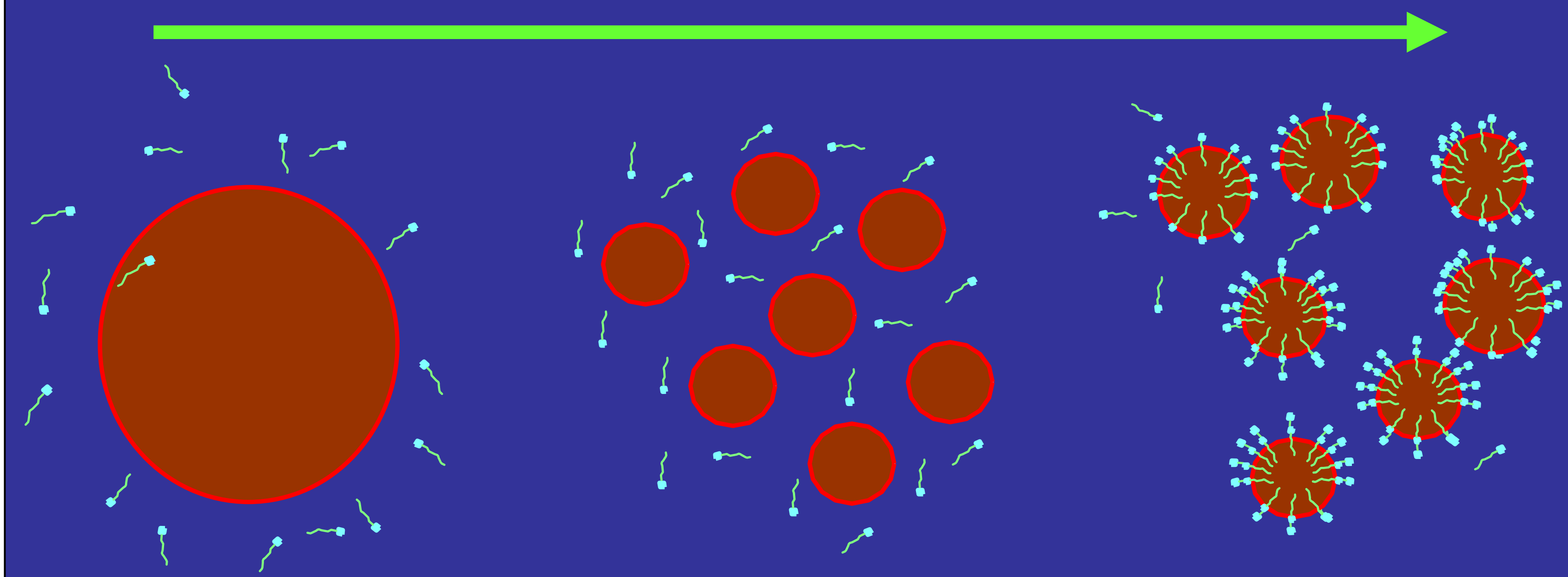
Emulsifiers in Emulsion Manufacture





Emulsification produces interface. 500 sq meters/liter.
Emulsifier reduces the interfacial energy and also provides charge

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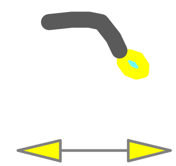
Emulsifier Molecules are very small!

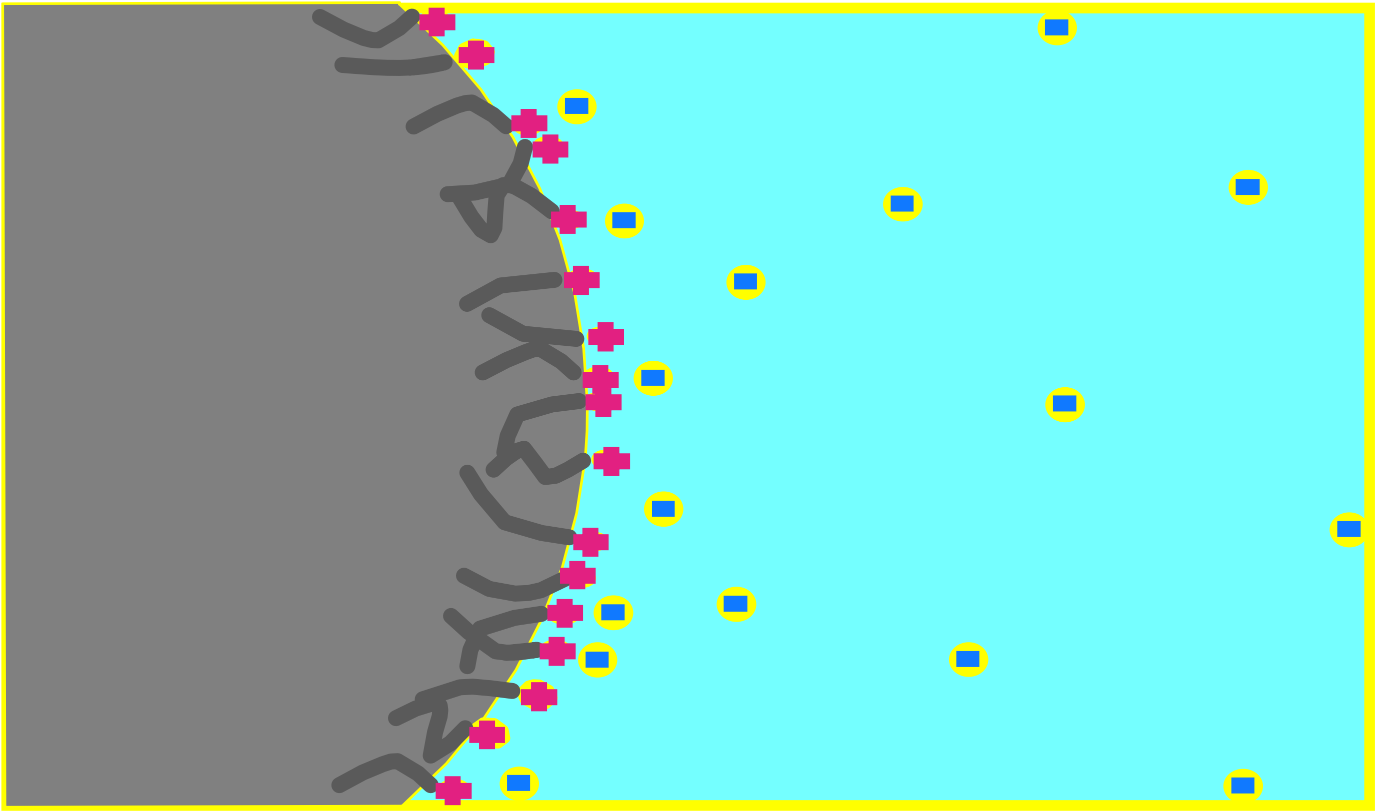
If an asphalt droplet were the size of the world, then the emulsifier head group would occupy an area of 4 square miles and the tail would penetrate 5 miles deep

asphalt droplet
diameter 3/1000 mm



emulsifier length
3/1 000 000 mm

Emulsifier generates charged Asphalt Droplets



Counterions diffuse into the water phase leaving the asphalt surface with a net positive charge

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Headgroup Charge and pH

Headgroups	Acid	Neutral	Alkaline
Sulphonate SO_3-	-	-	-
Ethoxylate $(C_2H_4O)_xH$	o	o	o
Carboxylate COOH/COO-	o	-	-
Amine NH2/NH3+	+	+	o
Quaternary Amine $N(CH3)_3$+	+	+	+
Asphalt	+	o	-
Mineral	+	o	-

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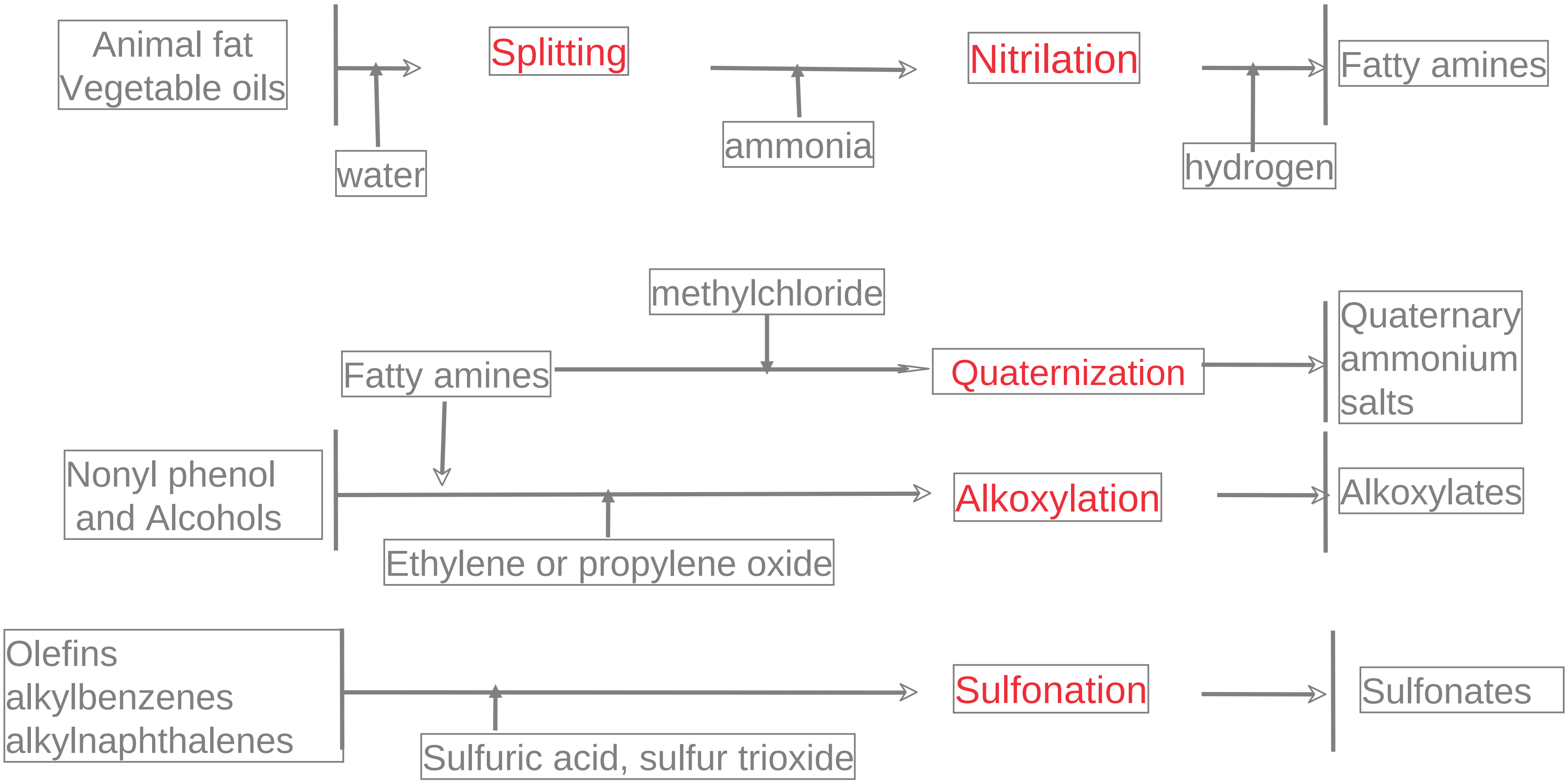
Manufacture of Emulsifiers



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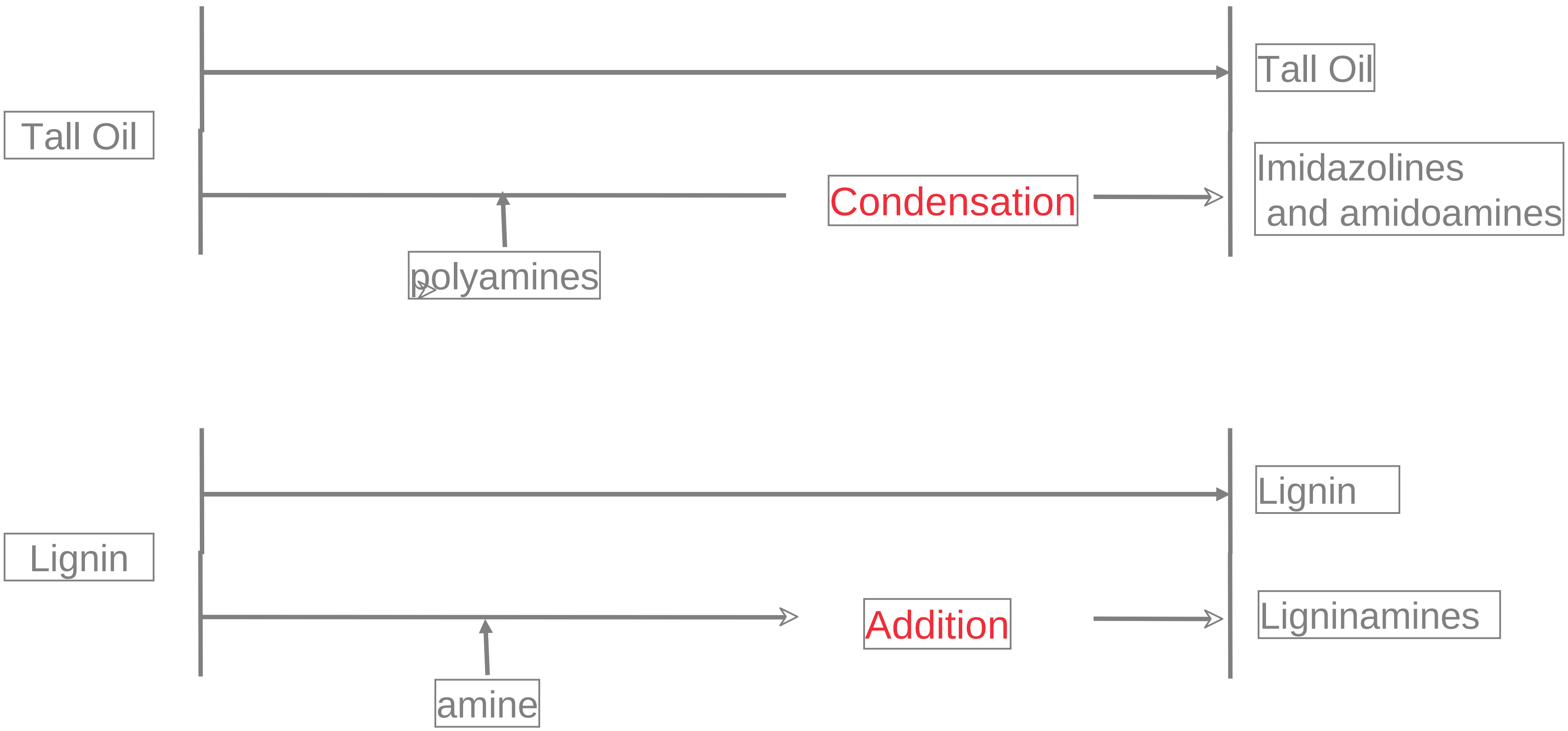
Manufacture of Emulsifiers



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Factors Affecting Breaking and Curing

- Aggregate Reactivity
  - surface area, surface charge, surface chemistry
  - filler chemistry e.g. cement, lime
- Emulsion Reactivity
  - emulsifier chemistry, concentration
  - other additives
  - asphalt viscosity
- Temperature, Humidity, Wind Speed
- Mechanical Treatment e.g.compaction

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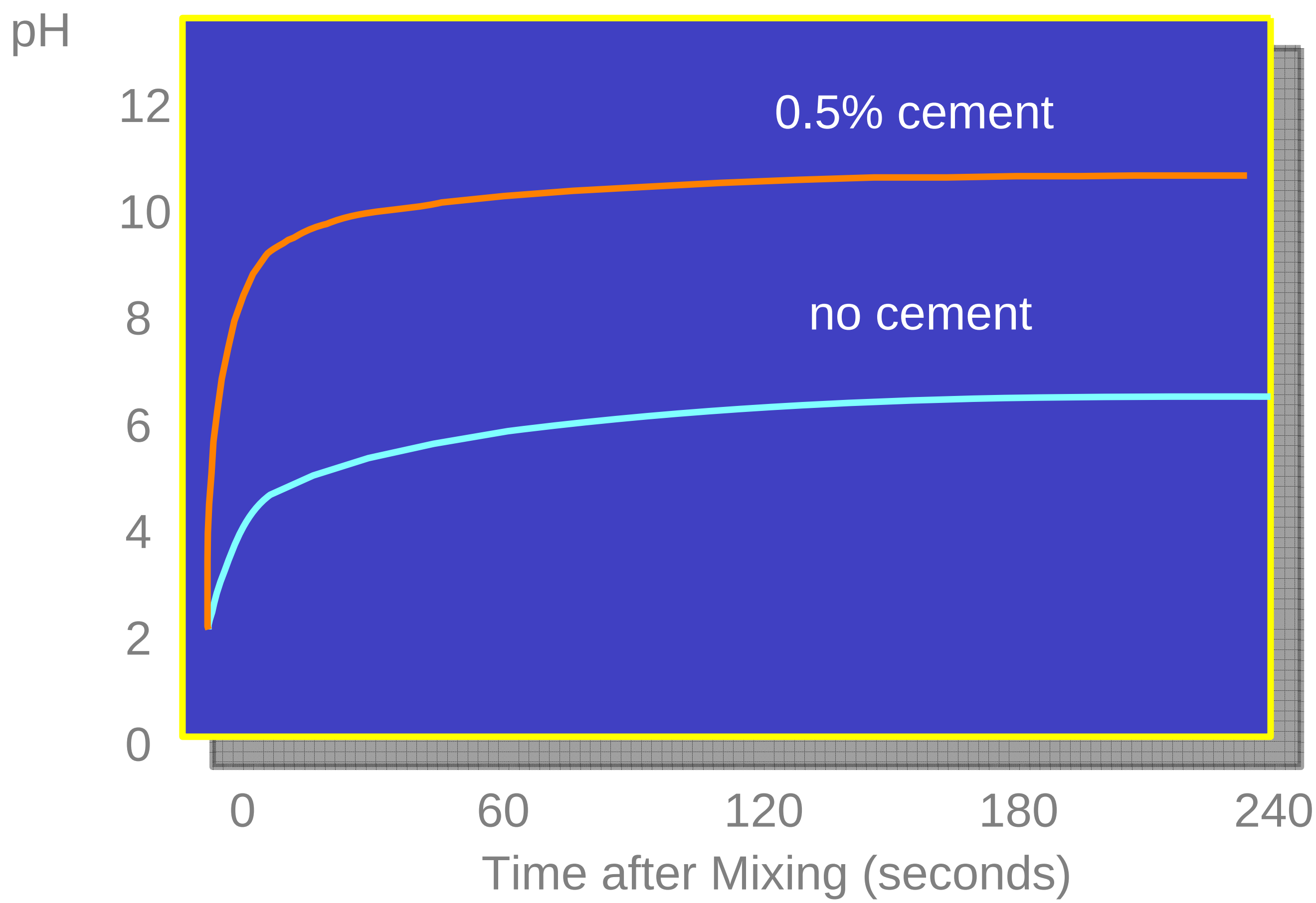
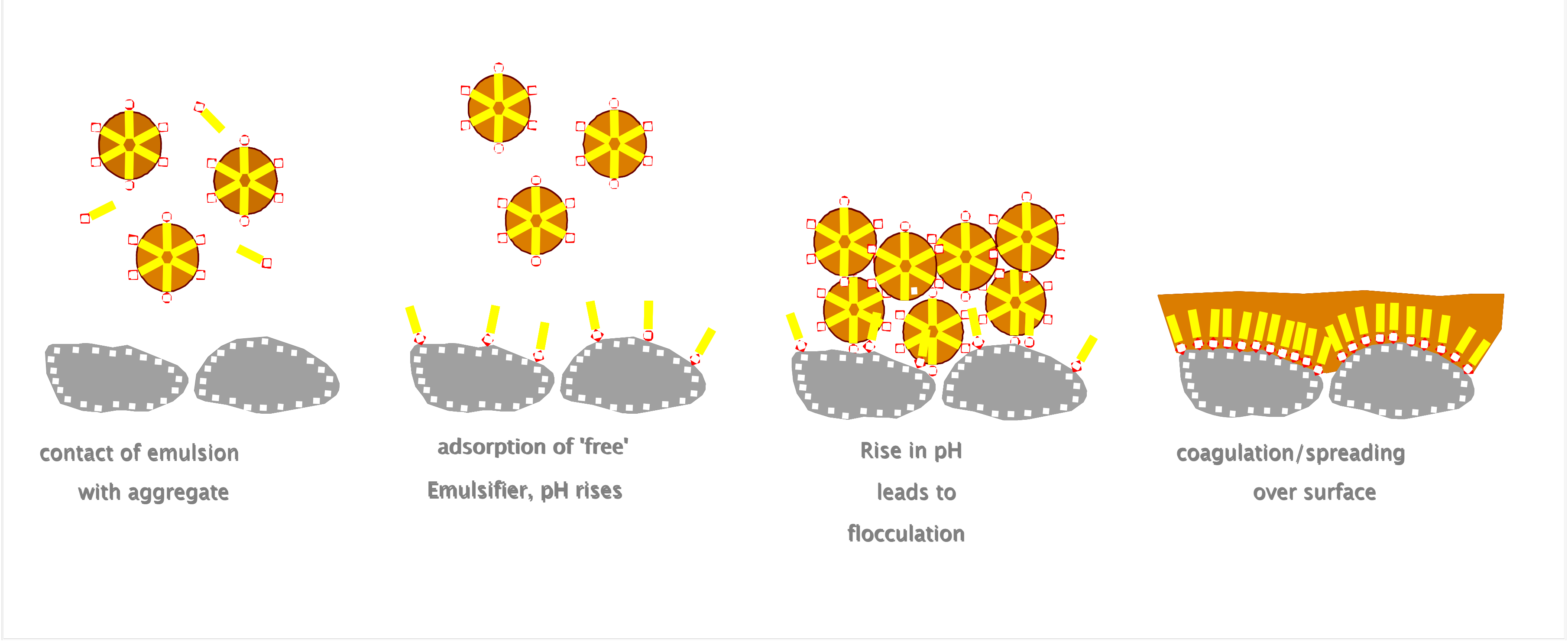
Setting Mechanisms Cationic Emulsions

- pH changes due to chemistry of aggregate or filler
- Heteroflocculation between emulsion droplets and oppositely charged mineral filler and aggregate
- Adsorption of 'free' surfactant onto aggregate.
- Absorption of water into porous substrates
- Evaporation of water

pH changes after mixing emulsion with Aggregate



Possible stages in cationic emulsion breaking



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Emulsifier Chemistry and Use Levels

	level %	typical emulsifiers
CRS	0.15-0.30	tallowdiamine
CMS	0.30-0.60	tallowdiamine
Micro	0.6-2.0	tallowtetramine, tall oil imidazoline
CSS	0.8-2.5	tallowdiquaternary, ethoxylates
RS	0.2-1.0	tall oil acids
MS	0.6-1.5	tall oil acids
SS	1.0-2.5	lignosulphonates, ethoxylates

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Other Emulsion Ingredients

- Polymer – modify binder properties
  - SBR, NR or PC Latex added via soap or asphalt
  - SBS, EVA polymer added via asphalt
- Solvents – modify binder properties
  - Naphtha, mineral spirits, No2 fuel oil, flux oils
  - added via asphalt, soap or to finished emulsion
- Rheology Modifiers – modify emulsion properties
  - Calcium or sodium chloride to reduce viscosity
  - water soluble polymers from cellulose, xanthan etc to increase viscosity and reduce settlement
  - Associative polymers like acrylates to increase viscosity
- Adhesion promoters, biocides, pigments

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Typical Cationic Emulsion Recipes

Soft asphalt for chipseal application

Asphalt 150pen	67	
Cationic latex	2.5	
Tallowdiamine	0.2	CRS-2P
Hydrochloric acid	0.1	
Calcium chloride	0.1	
Soap pH	2	
Water	to 100	
Asphalt	62	
Tallowdiquaternary amine [a]	1.2	CSS-1
Soap pH	6	
Water	to 100	

Typical Cationic Emulsion Recipes

Polymer modifier
Cationic type

CRS-2P

Asphalt 150pen	67
Cationic latex	2.5
Tallowdiamine	0.2
Hydrochloric acid	0.1
Calcium chloride	0.1
Soap pH	2
Water	to 100

CSS-1

Asphalt	62
Tallowdiquaternary amine [a]	1.2
Soap pH	6
Water	to 100

Typical Cationic Emulsion Recipes

Low concentration cationic emulsifier

Asphalt 150pen	67	CRS-2P
Cationic latex	2.5	
Tallowdiamine	0.2	
Hydrochloric acid	0.1	
Calcium chloride	0.1	
Soap pH	2	
Water	to 100	

Asphalt	62	CSS-1
Tallowdiquaternary amine [a]	1.2	
Soap pH	6	
Water	to 100	

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Typical Cationic Emulsion Recipes

Acid needed to activate emulsifier

Asphalt 150pen	67	
Cationic latex	2.5	
Tallowdiamine	0.2	CRS-2P
Hydrochloric acid	0.1	
Calcium chloride	0.1	
Soap pH	2	
Water	to 100	

Asphalt	62	
Tallowdiquaternary amine [a]	1.2	CSS-1
Soap pH	6	
Water	to 100	

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Typical Cationic Emulsion Recipes

To control viscosity

CRS-2P

Asphalt 150pen	67
Cationic latex	2.5
Tallowdiamine	0.2
Hydrochloric acid	0.1
Calcium chloride	0.1
Soap pH	2
Water	to 100

CSS-1

Asphalt	62
Tallowdiquaternary amine [a]	1.2
Soap pH	6
Water	to 100

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Typical Cationic Emulsion Recipes

Asphalt 150pen	67	
Cationic latex	2.5	
Tallowdiamine	0.2	CRS-2P
Hydrochloric acid	0.1	
Calcium chloride	0.1	
Soap pH	2	
Water	to 100	

High Dosage

Asphalt	62	
Tallowdiquaternary amine [a]	1.2	CSS-1
Soap pH	6	
Water	to 100	

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Typical Cationic Emulsion Recipes

Asphalt 150pen	67	
Cationic latex	2.5	
Tallowdiamine	0.2	CRS-2P
Hydrochloric acid	0.1	
Calcium chloride	0.1	
Soap pH	2	
Water	to 100	

No acid needed

Asphalt	62	
Tallowdiquaternary amine [a]	1.2	CSS-1
Soap pH	6	
Water	to 100	

QUESTIONS

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Testing and Specification of Emulsions

- Composition
  - Water, asphalt, solvent, polymer
- Handling and Storage
  - viscosity, storage stability (settlement), sieve
- Reactivity
  - demulsibility, cement mix test, filler index, mix tests
- Residue properties
  - penetration, softening point, float, ductility, torsional recovery, elastic recovery, PG grading(?),solubility
- Performance tests
  - adhesion, mix designs, application specific tests

Emulsion Properties – Performance Tests

- Adhesion/ Stripping Standard or Job Aggregate
- Coating Test Standard or Job Aggregate
- Sand Penetration Test for Tack, Penetrating Prime
- Mix Design for Cold Mix, Slurry Surfacing
- Sweep Test for Chip Seal
- Bond Strength for Tack Coat

	CRS-2	CMS-2	CSS-1	HFRS-2	HFMS-2	SS-1
Tests on Emulsions						
Viscosity at 25°C			20-100		100+	20-100
Viscosity at 50°C	100-400	50-450		75-400		
Storage stability 24 hours	<1	<1	<1	<1	<1	<1
Demulsibility	60+			60+		
Coating ability		Good/ fair			Good/ fair	
Particle charge test	positive	positive	positive			
Sieve test	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cement mixing test			<2			<2
Distillation residue	65+	65+	57+	63+	65+	57+
Oil distillate	<3	<12				
Tests on residue						
Penetration at 25°C	100-250	100-250	100-250	100-200	100-200	100-200
Ductility at 25°C	40+	40+	40+	40+	40+	40+
Solubility	97.5	97.5	97.5	97.5	97.5	97.5
Float test				1200+	1200+	

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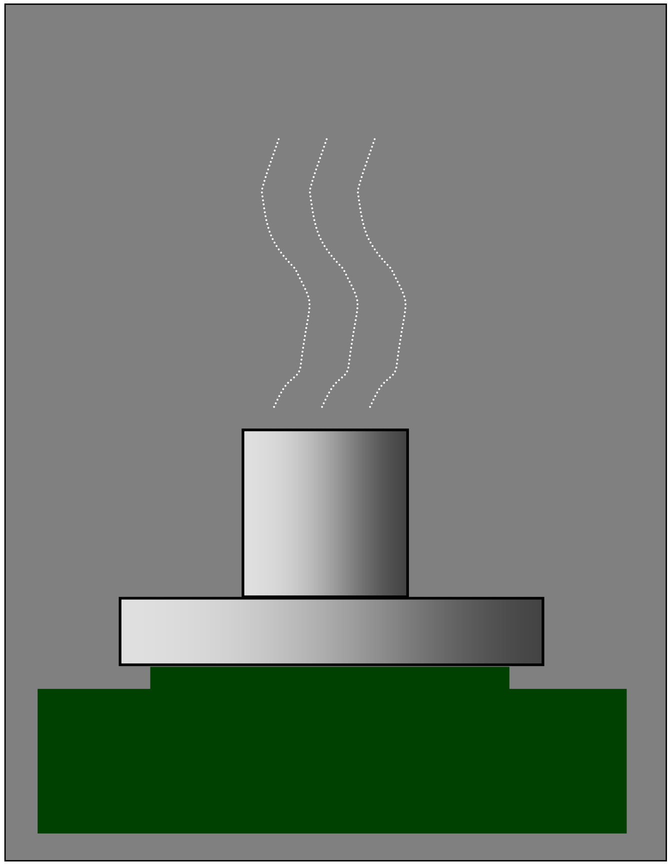
Measuring Residue content Rapid Boil Off Test



- 25g emulsion
- Aluminum can, anti-bumping granules
- Balance to 0.1g
- Time about 15 minutes
- Accuracy about 0.5%

Measuring Residue Content Distillation

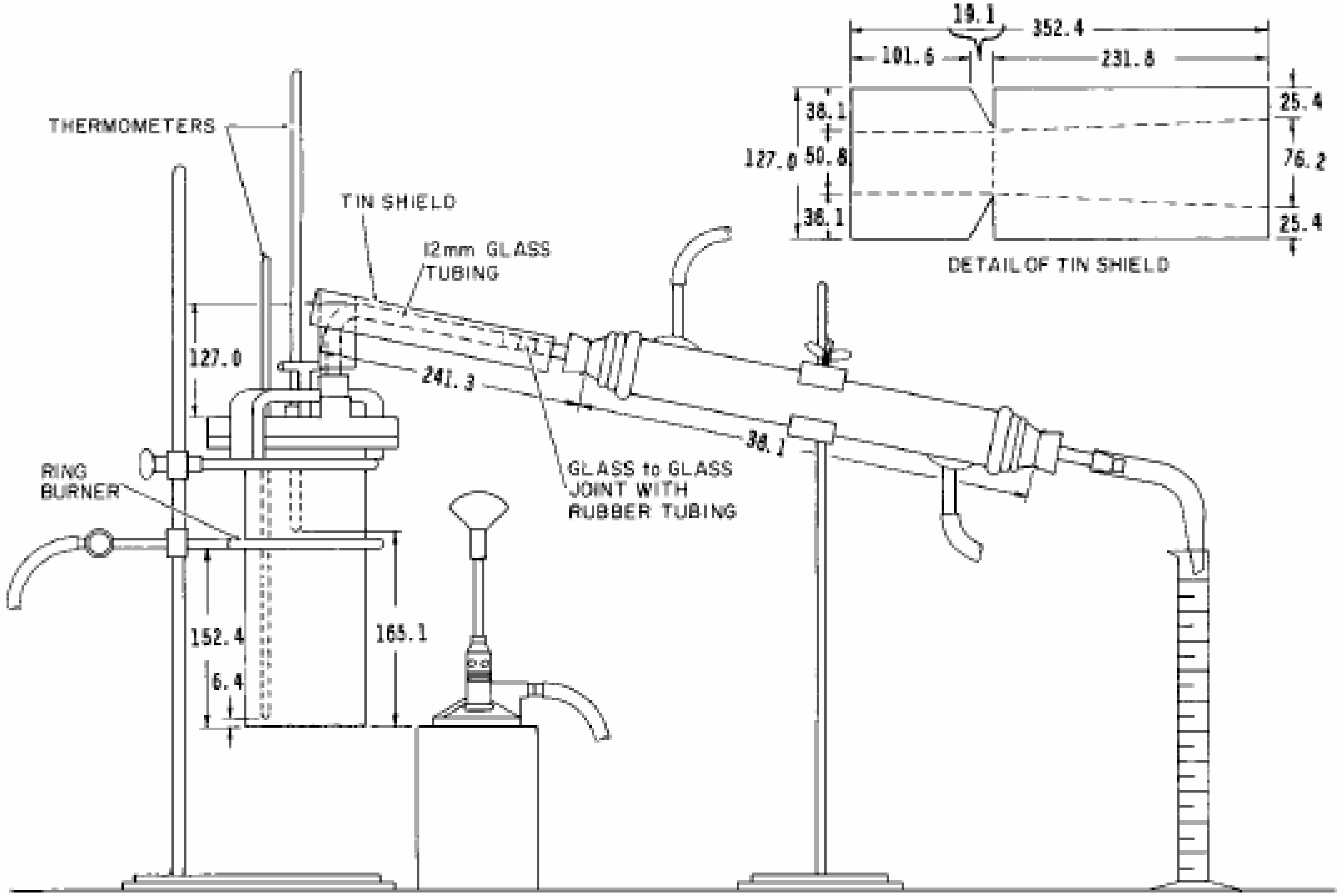
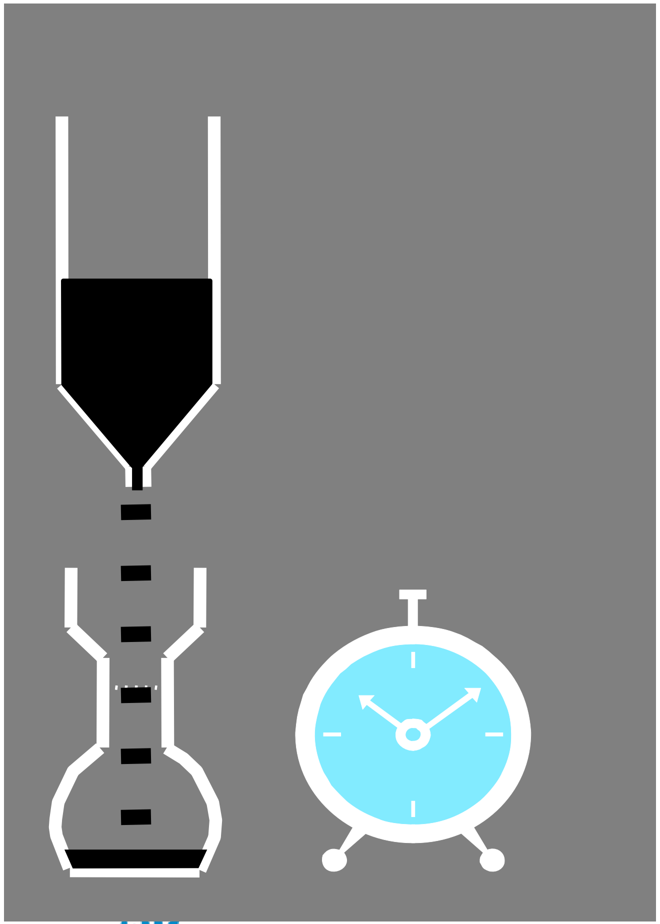


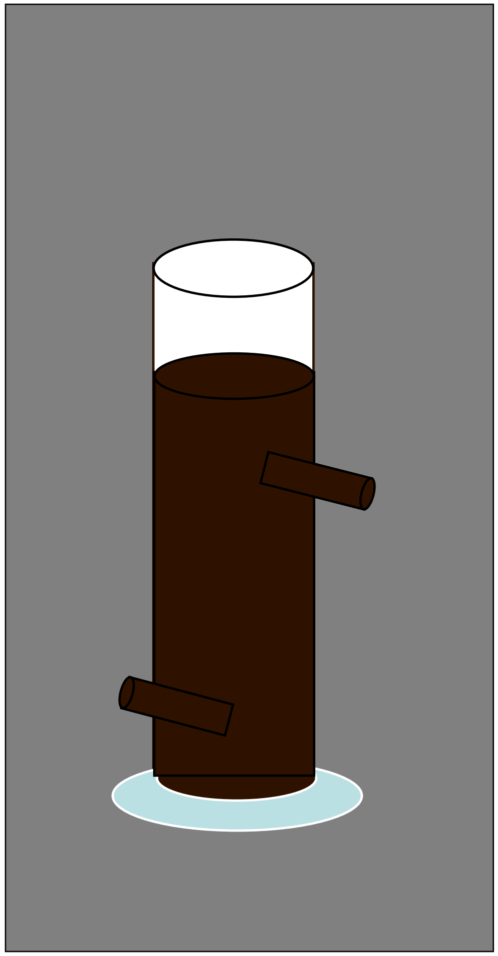
FIG. 3 Apparatus Assembly for Distillation Test of Emulsified Asphalts

Viscosity by Flow Cup



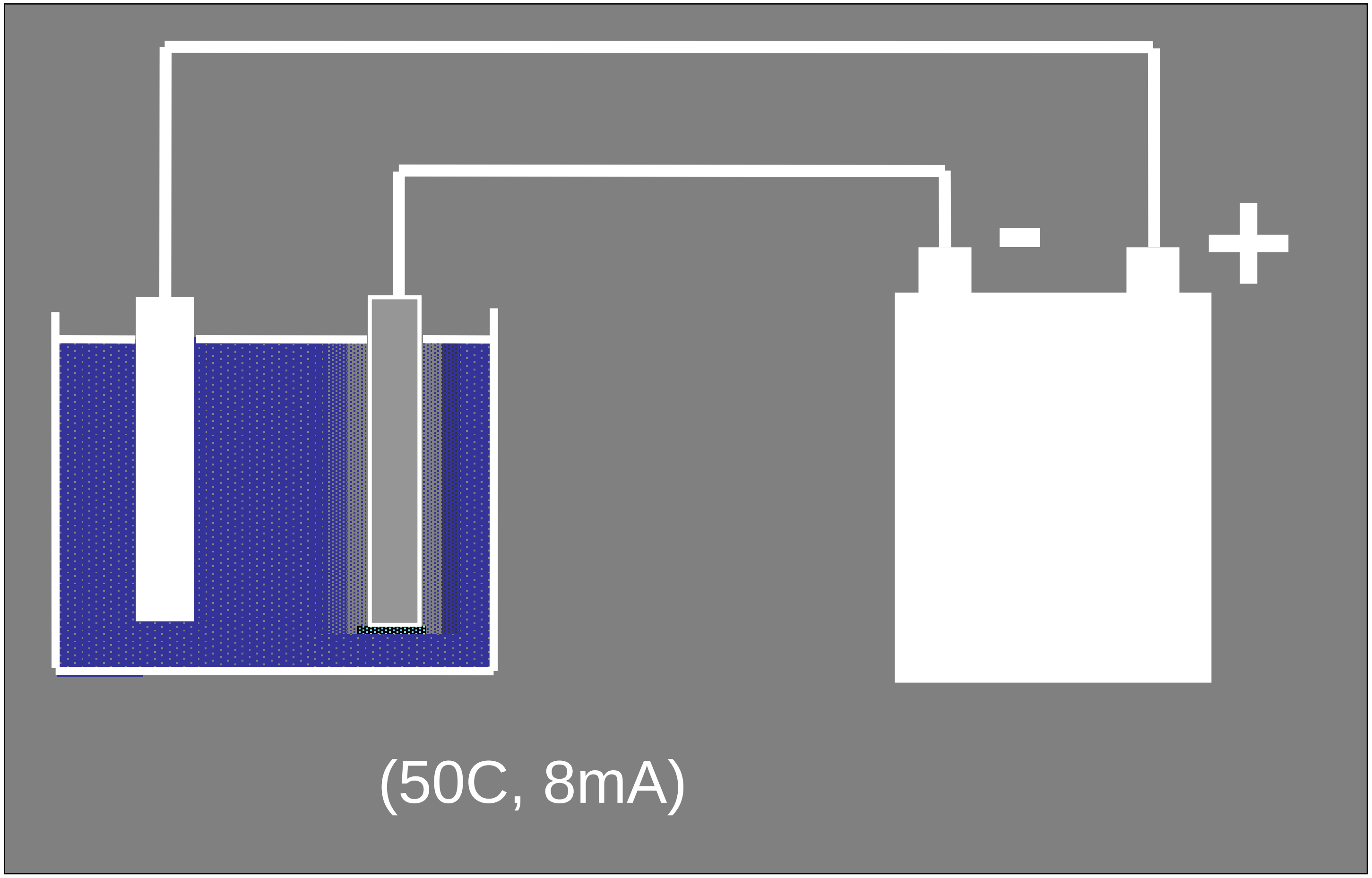
- 100ml emulsion (x 2)
- Viscometer cup and graduated flask
- Oil and water baths for temperature control
- Thermometers
- Stopclock
- Time taken about 30 minutes
- Accuracy ± 5-10%

Storage Stability and Settlement

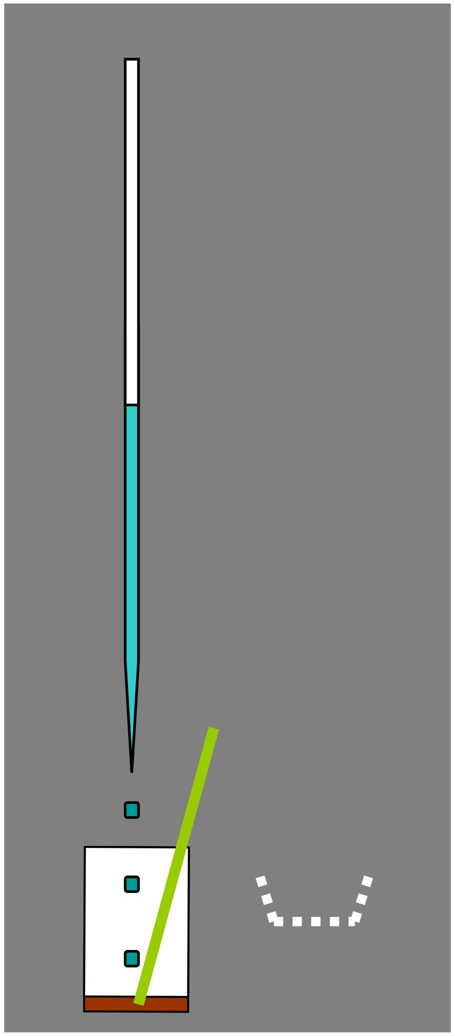


- 500ml glass measuring cylinder
- 500ml emulsion
- Time 1 or 5 days
- Residue on top and bottom portions
- Accuracy about 0.4%

Classification Tests
Particle Charge

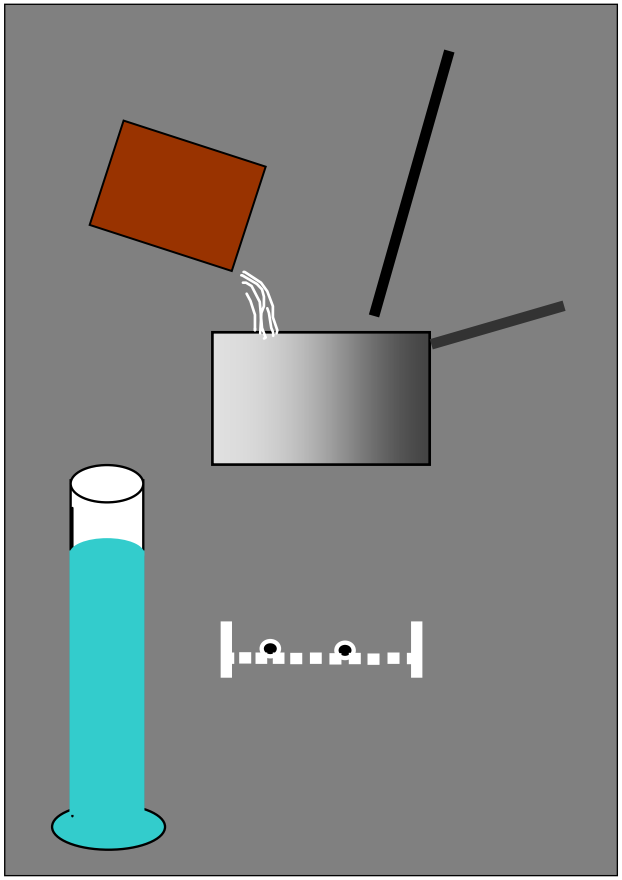


Classification Test
Demulsibility



- Burette + anionic soap solution to add 35ml over 2 minutes
- 100g emulsion
- 600ml steel beaker
- No 14 sieve cloth
- Hot Plate or oven
- stopclock and balance

Classification Test
Cement Mix Test



- Mixing bowl and rod
- 100g emulsion
- 50g cement
- 150g water
- Sieve, stopclock and balance

Applications of Emulsions

Spray

- Fog Seal
- Tack Coats
- Primes
- Pen Macadam
- Dust Control
- Chip Seal
- Scrub Seals

Mix

- Slurry Seal
- Microsurfacing
- Cold mix
- Warm mix
- Stabilization
- Cold recycling
- Coated Chips

Non-Paving

- Sealers
- Pipe Coatings
- Waterproofing
- Roofing
- Mulching
- Pelletization
- Crack Filler

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	Anionic			Cationic			
	Rapid Setting	Medium Setting	Slow Setting	Rapid Setting	Medium Setting	Slow Setting	Super-stable
Spray Applications							
Chipseal	✓			✓			
Fog Seal / Cement Curing		✓		✓	✓		
Tack Coat		✓ [a]	✓		✓ [a]	✓	✓
Prime			✓			✓	✓
Dust Palliative			✓				✓
Mulch			✓				✓
Penetration macadam				✓			
Industrial							
Waterproofing Coatings			✓ [c]				
Driveway & Footpath Sealers			✓ [c]			✓ [c]	

a) May contain up to 10% solvent b) Need not pass cement mix test c) May contain clay

	Anionic			Cationic			
	Rapid Setting	Medium Setting	Slow Setting	Rapid Setting	Medium Setting	Slow Setting	Super-stable
Plant Mixes							
Open-Graded/Semi Dense		✓[a]			✓[a]		
Dense-Graded			✓			✓	✓
RAP		✓				✓	✓
Stockpile Mix		✓[a]			✓[a]		✓
Pre-coated Chips					✓	✓	
Mix Paving							
Open-Graded					✓[a]		
In Place Mixes							
RAP		✓[a]			✓[a]	✓	✓
Dense-Graded			✓				✓
Soil Stabilization			✓				✓
Slurry Surfacing							
Slurry			✓			✓[b]	✓
Slurry for Capeseal			✓			✓[b]	✓
Microsurfacing						✓[b]	

a) May contain up to 10% solvent b) Need not pass cement mix test c) May contain clay

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New Applications and Developments

- Trackless Tack
  Emulsified high softening point / low pen asphalts
  Quick drying
  Can be trafficked without pick up
  Soften when hot mix overlay is applied to give good bond

- Penetrating Prime and Dust control
  Small particle size and wetting power helps penetration.
  Hard asphalts can give trackless properties.
  Quick to open
  Avoids volatile solvents in cut-backs or AEP recipes.

- Fog Seal for chip retention
  Reduced chip loss.
  Improved cosmetics
  Low cost

New Applications and Developments

- Warm Mix

Some techniques use emulsion technology for some of the largest temperature reductions. “Warmed –up” cold mix being used to get earlier cohesion in cold paving.

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Sources of Information

AEMA Asphalt Emulsion Manufacturers Association www.aema.org
AI Asphalt Institute www.asphaltinstitute.org
ISSA International Slurry Surfacing Association www.slurry.org
ARRA Asphalt Recycling & Reclaiming Association www.arra.org
NCPP National Center for Pavement Preservation www.pavementpreservation.org
Foundation for Pavement Preservation www.fp2.org
IBEF International Bitumen Emulsion Federation www.ibef.net

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