Some of the Open Issues in Modeling Asphalt

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Outline

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1. Asphalt Emulsions
2. Modified Asphalt
3. Aging of Asphalt

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Why is Asphalt Emulsion Necessary?

- Low temperature usage - Viscosity in the range of 0.5-10 Poise at 60°C when compared to 100-4000 Poise of Asphalt.
- Avoids oxidation of asphalt, reduced energy consumption, less hazardous
- Faster setting surface treatments, quick drying tack coats etc.
- 5 to 10% of asphalt consumption worldwide is related to emulsion application.
- More than 8 million tons of asphalt emulsion are produced (USA: 3 million tons of emulsion)

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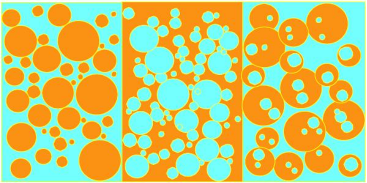

(a) (b) (c)

(*a*) O/W emulsion, (*b*) W/O emulsion, and (*c*) multiple W/O/W.

- An emulsion is a dispersion of small droplets of one fluid in another fluid.
- In most of the emulsion, one of the 'phase' is water.

- Standard asphalt emulsions are O/W type - 40 to 75% bitumen, 0.1 to 2.5 % emulsifier, 25 to 60 % water
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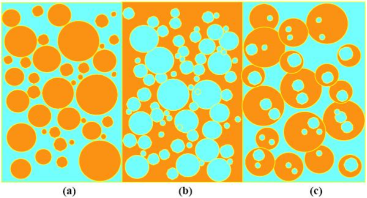

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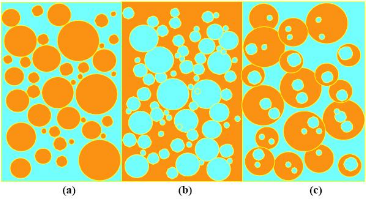

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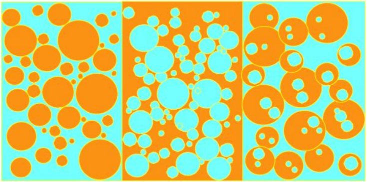

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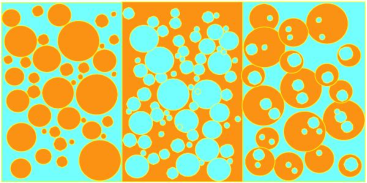

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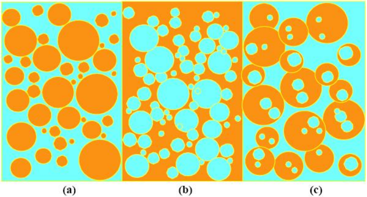

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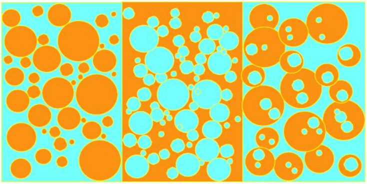

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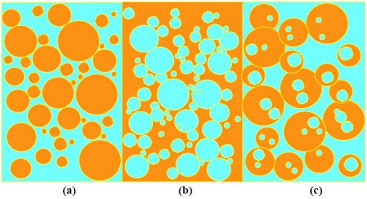

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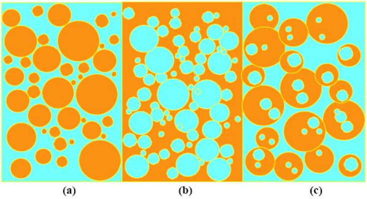

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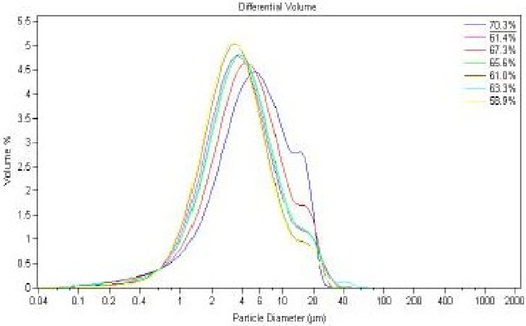

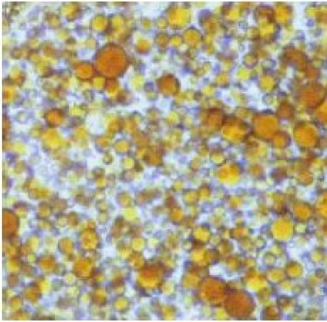

- Distribution of particle sizes in emulsion
- Depends on emulsion recipe, mixing conditions
- Large average particle sizes leads to lower emulsion viscosity.

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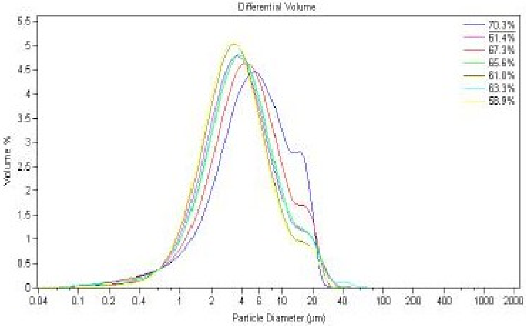

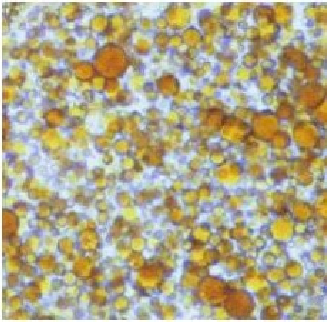

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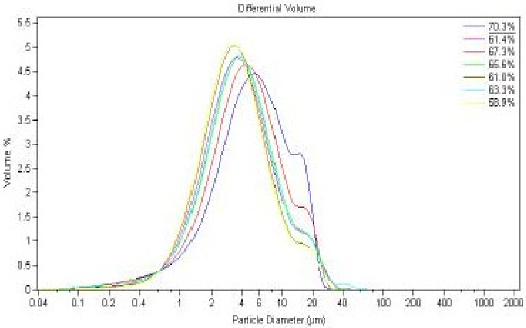

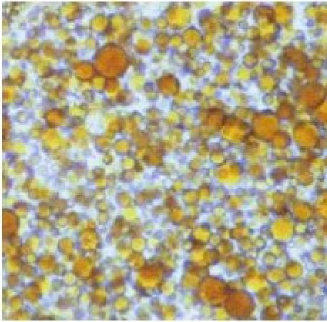

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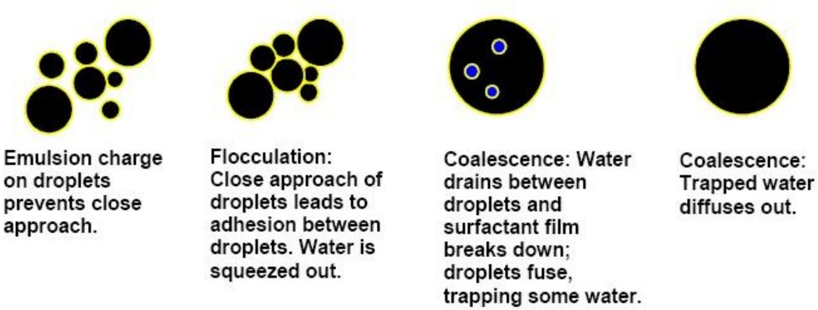
Breakdown of Asphalt Emulsion



- Macro-emulsions are inherently unstable, and over the period of time (hours to years), asphalt phase separates out from water (fusion of droplets - Coalescence).
- Asphalt droplets carry small charge, providing an electrostatic barrier. During mixing, rolling operations, the droplets overcome the barrier, and adhere to each other (flocculate).

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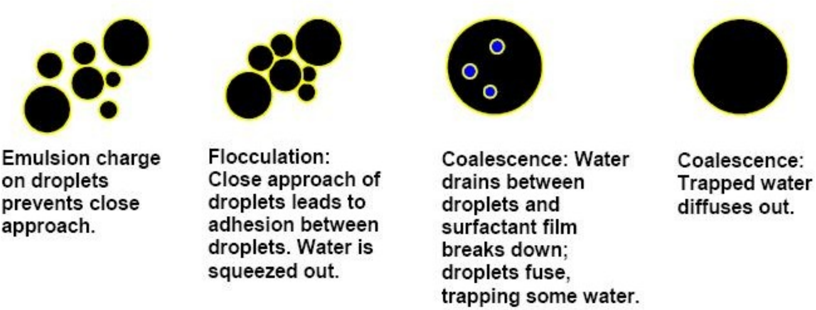

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Breakdown of Asphalt Emulsion

- Low viscosity asphalt coalesce more rapidly than high viscosity asphalt.
- Flocculation may sometimes be reversed by agitation, dilution or addition of more emulsifier, but coalescence cannot be reversed.
- Evaporation of water, settlement under gravity, freezing etc., accelerate the flocculation and coalescence process.
- Cationic, Anionic, Rapid-setting, Slow-setting, Medium-setting etc.

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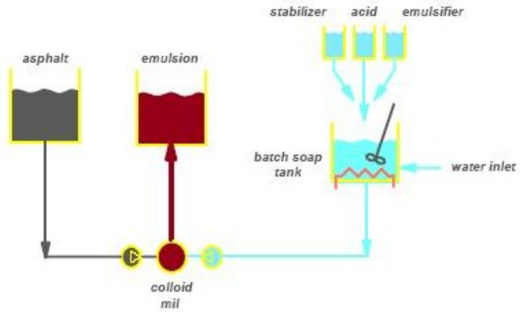
Manufacture of Asphalt Emulsion



- The emulsifier is dissolved in the water phase, and this ‘soap’ is mixed with hot bitumen in the colloid mill.
- Smaller droplets - high mechanical energy in the colloid mill, low bitumen viscosity and by the choice and concentration of the emulsifier (to reduce the interfacial tension).

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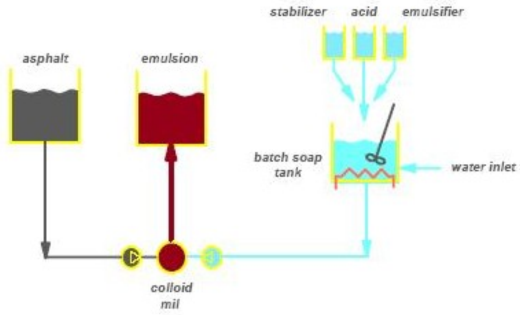

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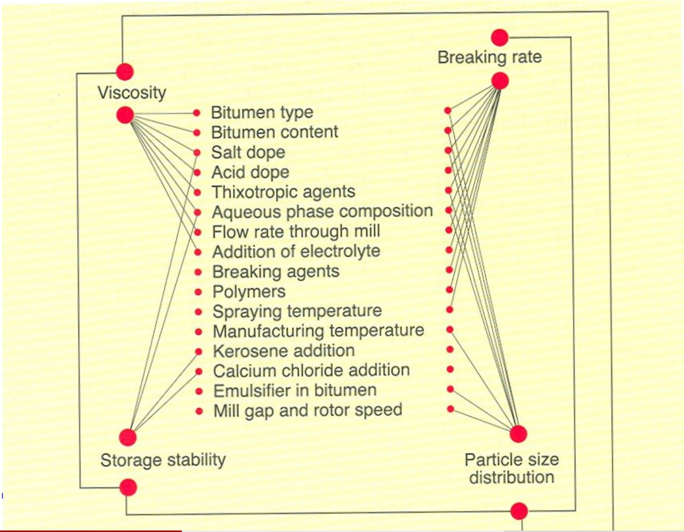
Complex Interrelationship between Manufacturing Variables and Emulsion Properties



Typical Emulsion Recipes

CRS		CSS		Anionic RS		Anionic SS	
Asphalt	65	Asphalt	60	Asphalt	65	Asphalt	60
Tallowdiamine	0.2	Tallow diquaternary ammonium chloride	0.6	Tall Oil	0.3	Ethoxylated nonyl phenol	0.5
Hydrochloric acid, 35%	0.15			Sodium hydroxide	0.2	Lignins	0.5
Soap pH	1.5–2.5	Soap pH	3–7	Soap pH	11–12	Soap pH	10–12
Water	to 100	Water	to 100	Water	to 100	Water	to 100

- Asphalt contains a small amount of salt, leading to ‘osmotic swelling’ of the droplets - Calcium or Sodium Chlorides are added to reduce the osmosis of water into bitumen.
- Solvent
- Polymers (??) - Polymer modified asphalt emulsion.

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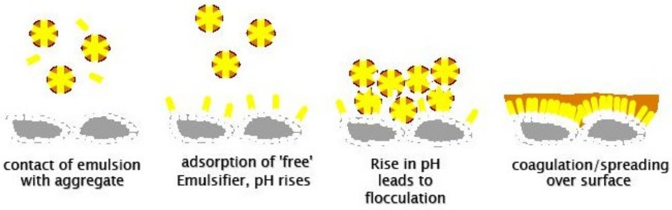

- Emulsified asphalt must revert to a continuous asphalt film in order to act as cement in road materials.
- Mechanism of setting and curing of asphalt emulsion still not elucidated clearly.
- Coalescence is a slower process and flocculation is a rapid process.
- Coalescence is an inverse process: the O/W emulsion is transformed into a W/O emulsion.

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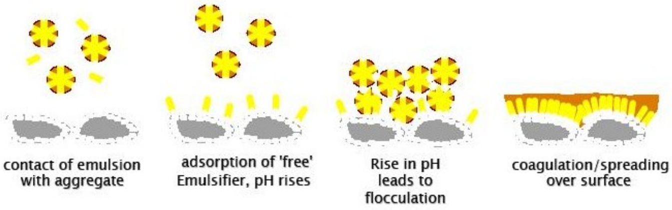

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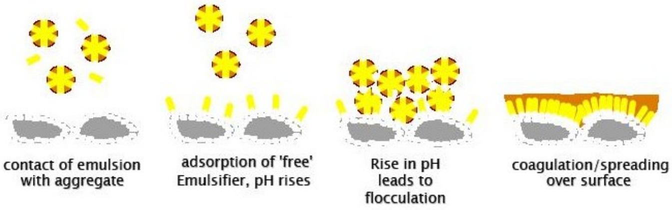

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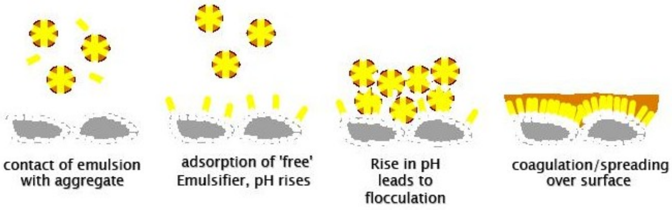

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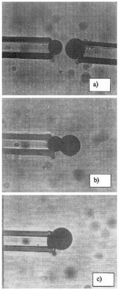

- This first nucleation step is followed by a shape relaxation driven by surface tension which causes the two droplets to fuse into a unique one.
- What will happen if the time separating two coalescence events is large compared to the ‘shape relaxation time’? (low droplet viscosity) - A gradual increase of the droplet size is observed.

- Coalescence consists in the rupture of the thin liquid film in between two adjacent droplets through the nucleation of a small channel

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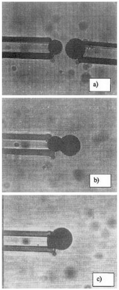

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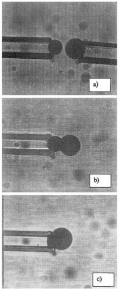

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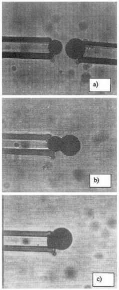

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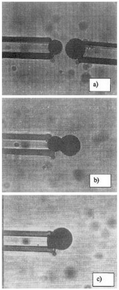

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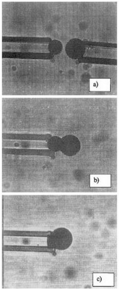

- Coalescence consists in the rupture of the thin liquid film in between two adjacent droplets through the nucleation of a small channel

- This first nucleation step is followed by a shape relaxation driven by surface tension which causes the two droplets to fuse into a unique one.
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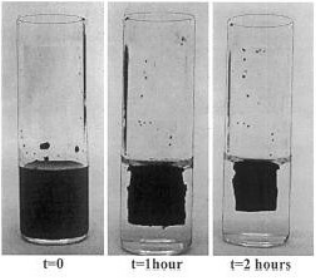

- A gel is initially formed made out of irreversibly connected droplets.
- The gel continuously contracts in order to reduce its surface area.
- When a destabilizing agent is added to the initially stable emulsion, it forms a gel, which contracts with time by preserving the geometry of the container.

- What will happen if the time separating two coalescence events is small compared to the 'shape relaxation time'?

Bonakdar et al.,(2001), Colloids and Surfaces, 176, 185-194.

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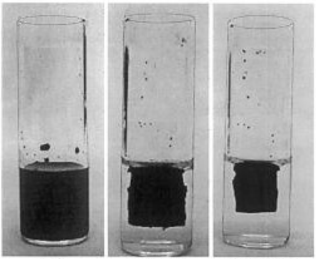

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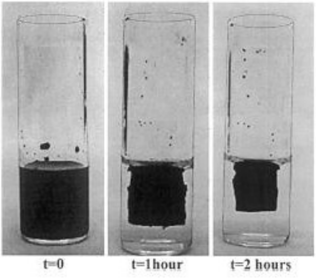

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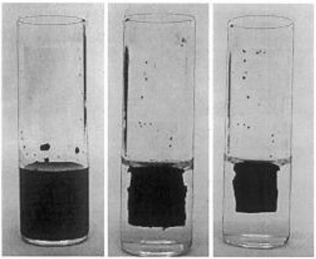

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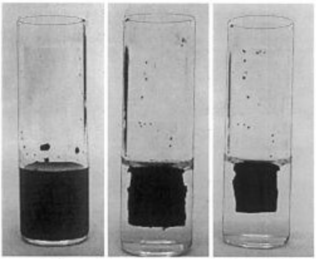

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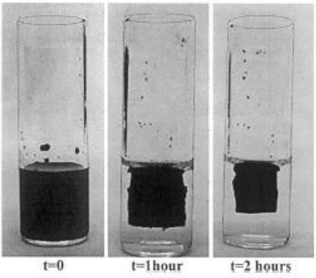

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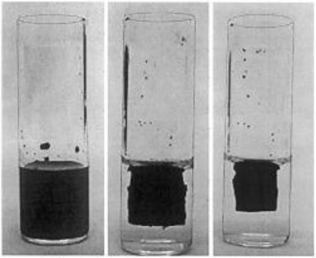

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Unanswered Questions - Asphalt Emulsions

- Rheology of Asphalt Emulsions - Extremely complex to test without breaking the emulsion
- Rheology of Asphalt Emulsions - Incidence of negative normal stress differences - Not reported till now
- Shape relaxation Vs. Flocculation
- Pressure dependent viscosity for emulsions - No measurement made till now!!!
- No constitutive model exists for emulsified asphalt mixtures

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Why modify?

- Currently available straight-run asphalts exhibit increased temperature susceptibility ('immature crude')
- Resistance to aging, load induced permanent deformation and cracking, low temperature cracking ...

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Different Types of Modifiers

Type of modifier	Example
Thermoplastic elastomers	Styrene–butadiene–styrene (SBS) Styrene–butadiene–rubber (SBR) Styrene–isoprene–styrene (SIS) Styrene–ethylene–butadiene–styrene (SEBS) Ethylene–propylene–diene terpolymer (EPDM) Isobutene–isoprene copolymer (IIR) Natural rubber Crumb tyre rubber Polybutadiene (PBD) Polyisoprene
Thermoplastic polymers	Ethylene vinyl acetate (EVA) Ethylene methyl acrylate (EMA) Ethylene butyl acrylate (EBA) Atactic polypropylene (APP) Polyethylene (PE) Polypropylene (PP) Polyvinyl chloride (PVC) Polystyrene (PS)
Thermosetting polymers	Epoxy resin Polyurethane resin Acrylic resin Phenolic resin
Chemical modifiers	Organo-metallic compounds Sulphur Lignin
Fibres	Cellulose Alumino-magnesium silicate Glass fibre Asbestos Polyester Polypropylene
Adhesion improvers	Organic amines Amides
Antioxidants	Amines Phenols Organo-zinc/organo-lead compounds
Natural asphalts	Trinidad Lake Asphalt (TLA) Gilsonite Rock asphalt
Fillers	Carbon black Hydrated lime Lime Fly ash

Benefits of Modification

Modifier	Permanent deformation	Thermal cracking	Fatigue cracking	Moisture damage	Ageing
Elastomers[80–82]	✓	✓	✓		✓
Plastomers[83,84]	✓				
Tyre rubber[85]		✓	✓		
Carbon black[86,87]	✓				✓
Lime[88,89]				✓	✓
Sulphur[90,91]	✓				
Chemical modifiers	✓				
Antioxidants					✓
Adhesion improvers				✓	✓
Hydrated lime[92]				✓	✓

Requirements of a Modifier

- Blend with bitumen
- Achieve coating or spraying viscosity at normal application temperature
- Physical and chemical stability during storage, application and in service
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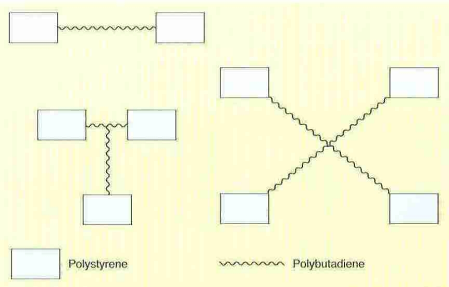
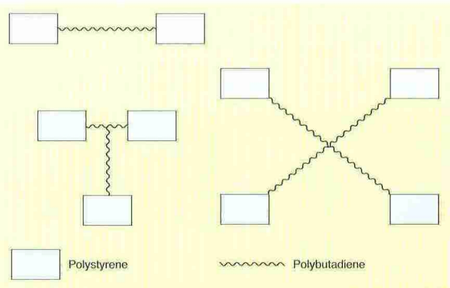
Modification with Thermoplastic Elastomers



- Styrenic block copolymers, radial or branched copolymers
- Quality of polymer dispersion
  - Constitution of bitumen
  - Type and concentration of polymer
  - Shear rate applied during the mixing process
- When polymer is added to hot bitumen, the bitumen penetrates the polymer particles causing the styrene domains of the polymer to become solvated and swollen

Modification with Thermoplastic Elastomers



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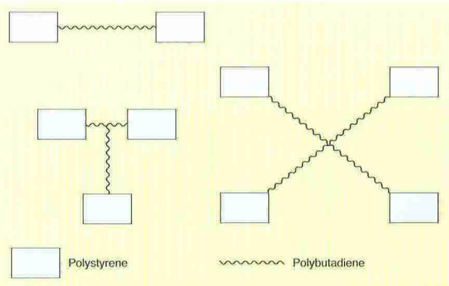

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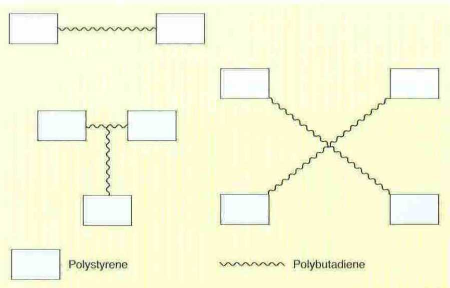

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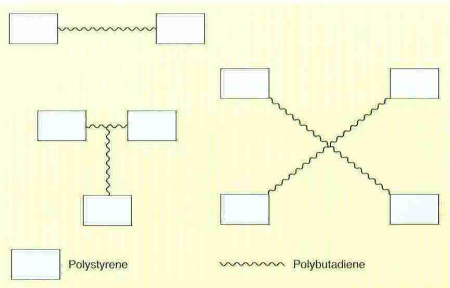

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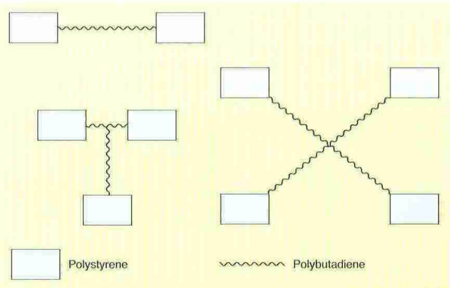

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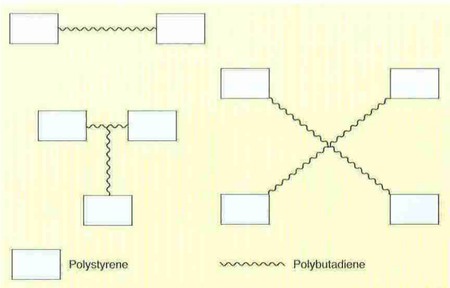

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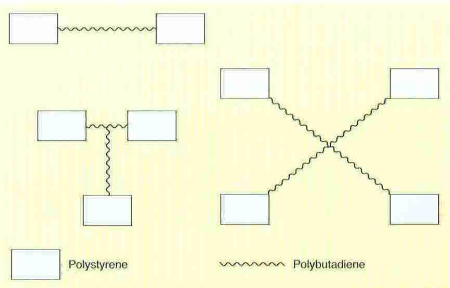

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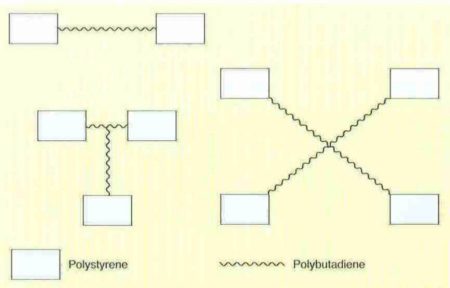

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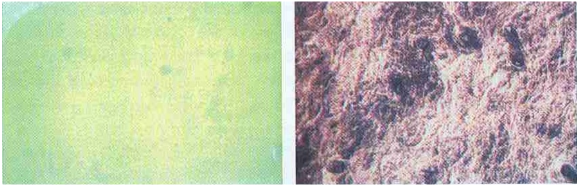

- Association of polar aromatics (resins and asphaltenes) depend on the solvency power of the saturates and aromatics in the maltenes phase of pure bitumen (the so called gel-like structure)
- Phase equilibrium of this complex mixture is disturbed due to the addition of thermoplastic elastomer (molecular weight similar to or more than asphaltenes)
- The polymer and the asphaltenes compete for the solvency power of the maltenes, insufficient maltenes leads to phase separation
- Compatible system has sponge-like structure whereas incompatible system has a coarse structure.

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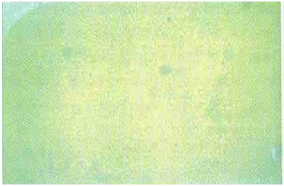

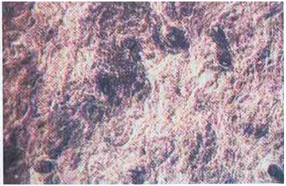

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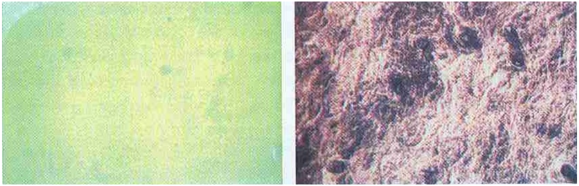

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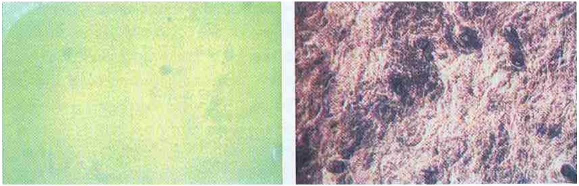

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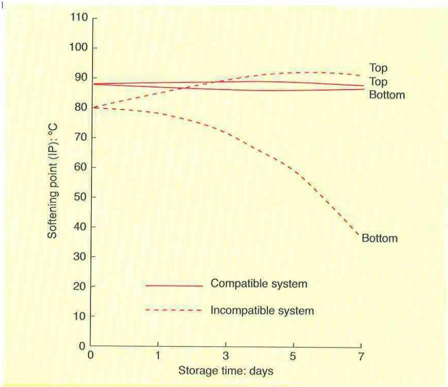
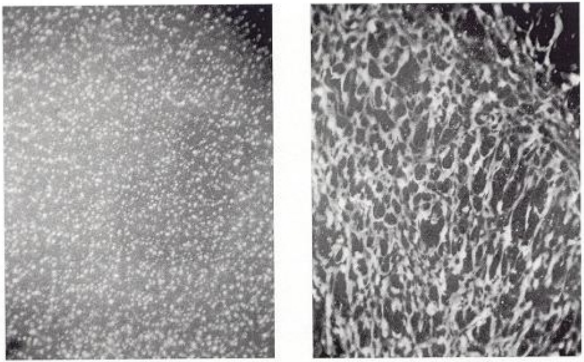


- Hot storage test to check for compatibility of the system.

Modification with Thermoplastic Elastomers



(A) B +3% SBS (B) B + 9% SBS

- Addition of more polymer results in asphalt in polymer solution.

Modification with Thermoplastic Elastomers

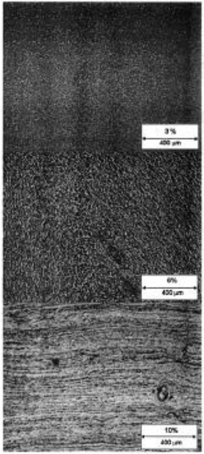


Figure 3. Dispersion of 3%, 6%, and 10% (w/w) of linear SBS (L1) in ABA as obtained by fluorescence microscopy. The lighter phase is polymer-rich, and the darker phase is bitumen-rich.

- At 6%, both phases are continuous.

Unanswered Questions - Modified Asphalt

- Constitutive Models for Modified Asphalt - No significant attempt till now
- What causes the stable/unstable behavior of bitumen-polymer blends?
- Compatibility of bitumen-polymer blends
- Aging of bitumen-polymer blends

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What is Aging?

"All bitumens undergo a more or less rapid change with aging that appears to be due to two or possibly more causes. Two distinct changes manifest themselves. One is the surface hardening, which is likely due to oxidation, and possibly to the volatilization of some light oils. It begins at the surface and gradually extends into the bitumen. The other is a hardening of the entire mass, evidently due to condensation of molecules. Both these changes take place in all bitumens, but one or the other may predominate. The former is much the less objectionable, as it makes but slow progress into the mass."

Dow (1903), Proceedings of the ASTM 6th Annual Meeting, 3, 349-373, Delaware.

Mechanism of Aging

“ When asphalt ages in the pavement, some of the oils and resins are preferentially absorbed into the pores of the aggregate, but the chief aging process is that of oxidation. Qualitatively, the oxidation changes experienced in the air-blowing still, in the hot mixer, and in the pavement are all of the same general nature. Over the course of the oxidation changes, the non-polar oils remain substantially constant, the resins decrease, and the asphaltenes increase. This indicates conversion of the smaller resin molecules to the larger asphaltene molecules. Undoubtedly, also, asphaltenes further combine with resins or themselves to still larger asphaltenes.”

Brown (1958), Proceedings of the Association of Asphalt Paving Technologists, 27, 171-176.

Mechanism of Aging

"…oxidation in dark, photooxidation under direct sunlight, volatilization, photooxidation under reflected light, photochemical action of direct light, photochemical action of reflected light, polymerization, age hardening, exudation of oil, changes by nuclear energy, action of water, absorption of oil by solid, absorption of asphaltic components at a solid surface, chemical reactions or catalytic effects, and microbiological deterioration."

Traxler (1963), Proceedings of the Association of Asphalt Paving Technologists, 32, 44-63.

Aging of Asphalt Vs. Asphalt Mixtures

- Laboratory simulation of aging of asphalt during mixing, laying and field conditions
- Aging in the presence of light and in dark
- Aging of Asphalt mixtures: Diffusion of oxygen into the pavement layers (air voids, thickness of asphalt film, type of aggregate particles . . .)

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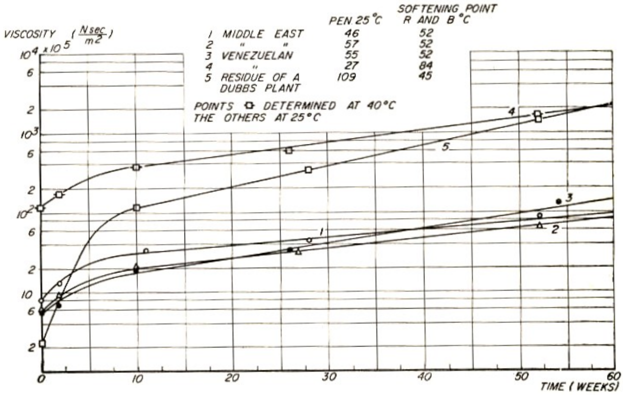
Oort's Investigation on Aging of Asphalt

- Oort (1954) experimentally studied the diffusion of oxygen using the classical diffusion equation and used the diffusivity and penetration of oxygen into asphalt films to correlate with the extent of aging.



Pressure Dependence on Aging of Asphalt

- Dependence of pressure on laboratory simulation of aging.

Condition	Asphalt 10: Viscosity, 77 F (megapoises)	Asphalt 10: Asphaltenes (%)
Original	1.70	12.9
Residue, TFOT	6.15	15.9
Vacuum, 24 hr	5.70	15.9
N_2, 1 atm, 24 hr	6.80	15.5
Air, 1 atm, 24 hr	7.20	16.3
O_2, 1 atm, 24 hr	10.0	16.9
O_2, 10 psig, 24 hr	10.5	16.4
O_2, 3 psig, 24 hr	11.0	17.6
O_2, 60 psig, 24 hr	12.5	17.7
O_2, 90 psig, 24 hr	14.0	18.0
O_2, 106 psig, 24 hr	-	-
O_2, 132 psig, 24 hr	14.5	19.2
O_2, 154 psig, 24 hr	15.4	18.5
O_2, 200 psig, 24 hr	17.8	19.4

Characterization of Aging

- Pavement Engineers rely on two laboratory tests for characterizing the aging of pure asphalt.
  Short term aging (rolling thin film oven) and Long term aging (pressure aging vessel/Microwave etc)
- Aging of Asphalt Mixtures: Hot mixture storage test
- No significant attempt has been conducted till now on modeling of aging of asphalt and asphalt mixtures.

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Open Issues in Characterizing Aging of Asphalt and Asphalt Mixtures

- A rigorous thermodynamic framework for modeling aging
- Modeling of aging of asphalt concrete layers - diffusion of oxygen into the porous pavement structure - Spatial and temporal change in the material properties
- Influence of pressure on aging of asphalt
- Interrelation between aging and healing of asphalt

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Thank you

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