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Chemically Modified Asphalt

Jack N Dybalski
Research Manager, Highway Chemicals Department, Akzo Chemie America

Asphalt is a highly complex residuum of crude oil which most technologists consider to be a natural colloid composed of two phases, dispersed and continuous.

The dispersed phase - the asphaltenes - can be described as high molecular weight, semi-polymeric, aliphatic/aromatic complexes which are present in asphalt as either discrete, uniformly dispersed particles, or flocculated or agglomerated electrostatically-bound clusters, or mixtures of both the discrete and flocculated forms.

The continuous phase, alternately referred to as the petrolene, malthene or oils-and-resins phase, have been the subject of some effort to analytically separate and characterize individual components. Selection of reagent sequence and analytical method determines whether 2, 3 or 4 components can be separated. The Rostler-Sternberg method separates the malthene or continuous phase into four components - Polar Aromatics, 1st acidaffins, 2nd acidaffins and Paraffins - by solvent and chemical precipitation. ASTM Method D-4124 (modified Corbett) separates tile continuous phase into three components - polar aromatics, naphthene aromatics and saturates by solvent extraction and alumina adsorption chromatography

During the past 30 odd years, these two methods have been the subject of considerable and repeated effort to relate asphalt performance factors to percentage ratios of the components of both the dispersed and continuous phase of literally hundreds of varying-source asphalts. These studies have demonstrated quite conclusively that neither good or poor in-service performance can be predicted by component ratio analyses.

Recent work utilizes an analytical procedure which can discern the degree of asphaltene dispersion and/or solution of asphaltenes in the continuous petrolene or malthene portion of an asphalt or blends of asphalts. A method devised and reported by Heithaus (ACS, September 1960) refers to this degree of dispersion or solution of asphaltenes as the 'state of peptization" which is an attempt to measure the interaction and compatibility of the components in paving and industrial grades of asphalt.

The method employs a small sample of asphalt dissolved in Toluene. Milliliter quantities of n-Heptane are measured from a burette into the Toluene solution of asphalt. Flocculation of the asphaltenes occurs at varying amounts of n-Heptane depending upon the source of the asphalt and the degree of asphaltene peptization. The flocculation end-point is microscopically observed.

This simplified version of Heithaus[1] method has been used by Akzo Chemie America for almost ten years to differentiate between asphalts from many different sources on their relative efficiency of cationic emulsification. As this work progressed and sufficient data was accumulated, most asphalts showed a good relationship between emulsion quality factors and the amount of n-Heptane required to reach the asphaltene flocculation end-point. The higher the amount of n-Heptane required to reach the flocculation end-point the better the emulsion quality factors became.

The polar aromatic component of asphalt, found to contain basic nitrogen constituents, is believed to be most responsible for the natural peptization of asphaltenes. They are believed to be adsorbed by the asphaltenes which implies some degree of electrochemical solvating interaction between these two components and the remaining petrolene or malthene fractions. Charge intensity characterization of the asphaltenes isolated from either the Corbett or Rostler methods indicates a negative charge of low intensity determined by Zeta Potential. The negative charges range from -14 mv to -33 mv depending upon the source of the asphalt. It is not known whether action of the precipitating solvents and additional handling required in the separation methods affect the electrochemical charge of the asphaltenes. However, it has been known for some years that sharing cationic asphalt emulsifiers between the molten asphalt phase and the water phase prior to emulsification tends to improve many of the finished emulsion properties such as particle size, viscosity and settlement. An extension of this work led to the evaluation of several cationic chemical classes and types as pretreatments for asphalt and blends of asphalt based upon their selective adsorption by the asphaltenes in the neat asphalt and affecting their degree of peptization.

Some chemicals from the study possess the ability to augment the peptization of the asphaltene component of many asphalts now in use. While the degree of response to chemical treatnent bv asphalts from different sources does vary, some improvement in temperature susceptibility, oxidation resistance, ductility, aged residue viscosity ratio and emulsification factors has been acted.

Over 80% of nearly 100 asphalts tested have been beneficiated to some degree.

Unfortunately, the Heithaus method, because of the eluting effect of Toluene on the chemical treatments, cannot be used to determine the beneficial effect of the chemical pretreatments of asphalt. The degree of beneficiation must be determined by the individual test methods available for each performance property.

Table I indicates the differences noted in some emulsion quality factors between asphalts with varying degrees of asphaltene peptization based upon a modified Heithaus titration.

Tables II and IIA reflect the benefits gained in quality emulsion factors by chemically pretreating the base asphalt.

Tables III and IV reflect the beneficiation of asphalt cement by chemical treatment.

TABLE I : Emulsion Properties related to Flocculation End Point.

Asphalt	Flocculation End Point ml	Emulsion Type , and % asphalt	Particle Size Distribution (2)		Viscosity SSF @122F		Settlement %	
			%	Micron	Static	Stirred(3)	5 days	21 days
33	23	CRS-2 (68.5%)	27	<1	157	92	4.4	16.8
			51	1-10				
			22	>10				
4	38	CRS-2 (68.3%)	41	<1	192	119	1.9	6.6
			47	1-10				
			12	>10				
23	69	CRS-2 (68.3)	86	<1	353	276	0.6	1.7
			14	1-10				

1) All emulsions 0.22% emulsifier
2) Levy-Hausser Counting Chamber
3) Mechanically stirred after 16-18 hours static , @122F. Rerun after 1 hour static.

Table II : Effect of Chemical pretreatment on Emulsion Properties

Asphalt	Emulsion Type	Chemical treatment*	Particle Size Distribution Untreated		Particle Size Distribution Treated	
33	CRS-2 (68.5%)	C	27	<1	59	<1
			51	1-10	38	1-10
			22	>10	3	>10
33	CRS-2 (68.5%)	G	27	<1	48	<1
			51	1-10	44	1-10
			22	>10	8	>10
4	CRS-2 (68.3%)	C	41	<1	71	<1
			47	1-10	26	1-10
			12	>10	3	>10
4	CRS-2 (68.3%)	G	41	<1	62	<1
			47	1-10	37	1-10
			12	>10	1	>10

*0.2% basis asphalt

TABLE IIA : Effect of Chemical Pretreatment on Emulsion Properties

Asphalt	Emulsion	Chemical treatment*	Viscosity SSF 122F		Settlement % 21 days	
			Before	After	Before	After
33	CRS-2 (68.5%)	C	157(92)	284(210)	16.8	3.6
33	CRS-2 (68.5%)	G	157(92)	277(208)	16.9	2.9
4	CRS-2(68.3%)	C	192(119)	362(318)	6.6	0.8
4	CRS-2(68.3%)	G	192(119)	385(327)	6.6	0.4

*0.2% basis asphalt

TABLE III: Effect of Chemical pretreatment on Asphalt Properties - Ductility

Ductility:	Untreated		Chemical Treatments (After)		
Asphalt	Before	After	C	G	J
4	150+	33	80	84	62
9	150+	16	79	69	80
12	150+	64	120	111	97
21	150+.	26	79	61	64
23	150+	59	84	89	60
33	150+	28	74	71	64
46	150+	25	68	84	53
58	150+	18	51	49	57
77	150+	58	81	89	72
81	150+	37	71	79	70

After RTFOT, ASTM D-2872 , 325 F., 75 minutes

TABLE IV : Effect of Chemical Pretreatment on Asphalt properties- Ageing Index

	Ageing Index			
Asphalt	Untreated	Chemical Treatments		
		C	G	J
4	4.71	1.88	1.68	2.12
9	7.42	3.40	3.68	3.98
12	2.17	1.68	1.72	1.56
21	5 53	2.86	3.65	3.68
23	2.77	1.44	2.84	1.66
33	6.64	3.96	5.96	4.22
46	6.20	5.44	4.82	4.20
58	8.10	6.14	6.92	5.20
77	2.87	2.25	2.08	2.03
81	4.80	2.88	3.02	3.45

Ageing Index - Ratio of viscosity, ASTM D-2171 Before and After RTFOT, ASTM D-2872

SUMMARY

1. Certain oil-soluble cationic surfactants are selectively adsorbed by the negatively charged asphaltene component in asphalt. Precipitation of asphaltenes with solvents such as n-Heptane or n-Pentane followed by elution with Isopropyl or Ethyl Alcohol reveal more than 50% of the cationic surfactant originally added to the asphalt is carried by the asphaltenes.
2. Certain cationic surfactants are more highly positively-charged than the naturally occurring Polar Aromatic component of asphalt as determined by Zeta Potential. These cationic surfactants tend to be adsorbed by the asphaltenes in preference to the Polar Aromatics.
3. There is a relationship between some performance factors of most paving-grade asphalts and the degree of peptization of the asphaltenes as determined by a modified Heithaus method using a simple one-step titration.
4. It is inferred that selective adsorption of certain cationic surfactants by the asphaltenes more efficiently redisperse the asphaltenes throughout the continuous phase. The net effect is improvement of some of the performance factors of asphalt.
5. Not all asphalts respond to chemical treatment to the same degree

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CONCLUSIONS

1. Selective chemical treatment of asphalt can improve many of its performance factors.
2. Emulsification factors such as particle size and distribution, viscosity and settlement can be improved.
3. Ductility and Ageing Index of chemically treated asphalt cements are improved with the majority of paving asphalts used in the U.S.