Asphalt Fractional Composition: Correlation Between Rostler and Clay-Gel Components

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ABSTRACT

Considerable data have been accumulated in studies sponsored by the FHWA and other agencies that were intended to relate pavement performance to asphalt fractional composition as determined by the Rostler acid precipitation method. Newer fractional compositional analysis methods are available that have some advantages such as retention of components after fractionation for other testing of these individual fractions. One of these methods is modified clay-gel column chromatography as described in this paper. The intent of this study was to determine if a relationship exists between fractional composition as determined by the two different methods in order to use previously obtained Rostler data for current studies of performance of recycled asphalts. Thirty-one combinations of asphalt recovered from aged pavements blended with recycling agents were analyzed for fractional composition by the Rostler and modified clay-gel methods. Regression analyses were conducted to relate clay-gel compositional parameters to Rostler composition. Results of this study indicate that workable relationships between fractional composition as determined by two methods exist and that reasonable predictions of clay-gel fractional composition can be made from Rostler compositional data. Use of these relationships can be made in many studies of recycling agents and recycled asphalts and for several other applications in which Rostler fractional composition is related to asphalt pavement performance.

Asphalt chemical composition in the study of asphalt performance and characteristics has received more attention in recent years as recycling agents and other asphalt characteristics that affect pavement performance have been investigated.

Several methods of fractional composition have been used and proposed (1) in recent years. At least two have been published as ASTM Standard Methods (D 2006 and Proposed Methods for Asphalt Composition Analysis, Vol. 04.03, 1983).

Considerable work has been conducted by the Federal Highway Administration (2-4) using the Rostler method of fractional composition. Among the information generated in these studies are data that could be used to relate pavement performance characteristics to asphalt composition.

Another method based on clay-gel chromatography has recently been developed and is receiving considerable attention by several pavement agencies. The method is straightforward and repeatable, but sufficient data have not been accumulated to attempt to relate pavement performance to fractional composition as determined by the clay-gel method.

The intent of this study was to investigate the possibility of the existence of correlations between fractional composition as determined by the two methods in order to more effectively evaluate recycling agents. A second objective was to test the ability of the clay-gel method to predict composition of blends of asphalt materials when the composition of the constituents is known.

MATERIALS

This study used 31 asphalt materials previously used in a study of recycling agents and recycled asphalt. Included are two asphalts extracted from aged pavements that were recycled, several recycling agents, and several combinations of these aged asphalts and recycling agents.

Clay-gel compositional analysis was performed on the materials at the New Mexico Engineering Research Institute Laboratories and Rostler compositional analysis was conducted by the laboratories of Matrecon, Inc., of Oakland, California.

METHODOLOGY

Both methods separate asphalt into two primary constituents. Asphaltenes are precipitated from the asphalt with n-pentane and the maltene fraction remains in solution. Both methods use the same fractionation technique to separate asphaltenes from maltenes, and the study shows that asphaltene concentrations are the same for each method.

The maltene fraction is further reduced to four fractions by the Rostler method and to three fractions by the clay-gel method.

The Rostler method of fractionation consists of reacting the maltenes with increasing concentrations of sulfuric acid. A flow diagram of the method is shown on Figure 1. Rostler fractions recovered (in order of increasing paraffinicity or decreasing reactivity with sulfuric acid) are

* Nitrogen bases,
* First acidaffins,
* Second acidaffins, and
* Paraffins.

The clay-gel method of fractionation consists of separation by adsorption on Attapulgus clay and silica gel columns with removal by selected solvents. The method is a modification of a proposed ASTM
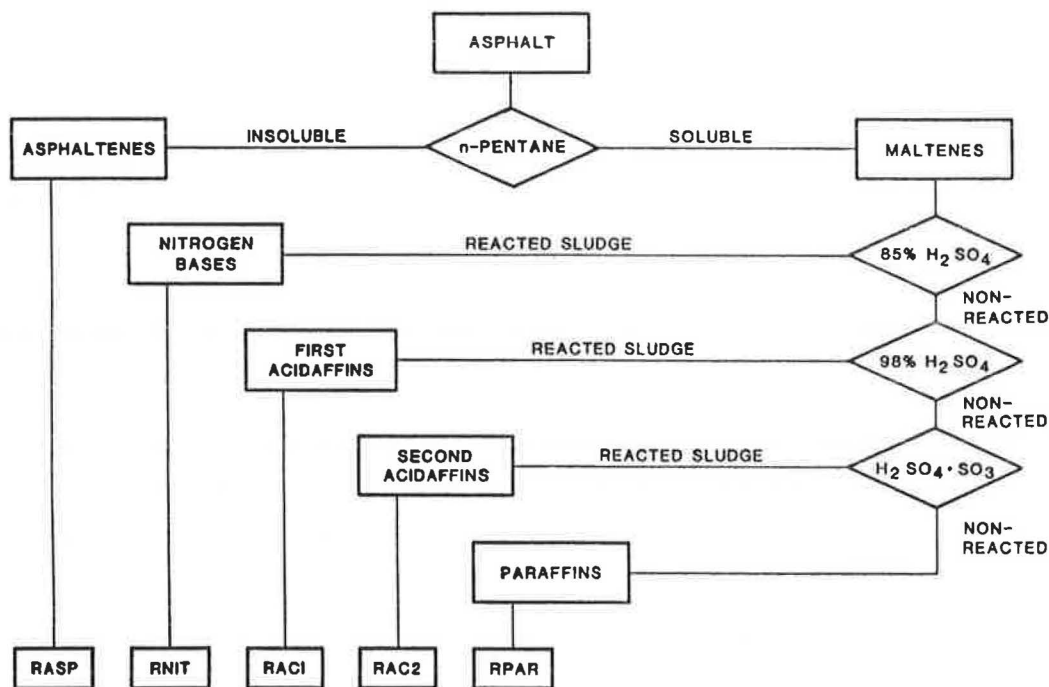
FIGURE 1 Schematic, Rostler separation.

Standard. Modifications are described later and a flow diagram of the method is shown in Figure 2. Fractions recovered (in order of decreasing polarity) are

- Polars,
- Aromatics, and
- Saturates.

In comparing the four maltene fractions of the Rostler method with the three fractions of the clay-gel method (Figure 3), an approximate linear relationship between the fractions was assumed. The clay-gel saturates probably consist mostly of Rostler paraffins; the clay-gel polars probably consist mostly of Rostler nitrogen bases and some first acidaffins; and the clay-gel aromatics probably contain both Rostler first and second acidaffins and perhaps traces of the other Rostler fractions. The General Linear Model (GLM) regression analysis of the SAS Institute ($\underline{5}$) was used for the analysis.

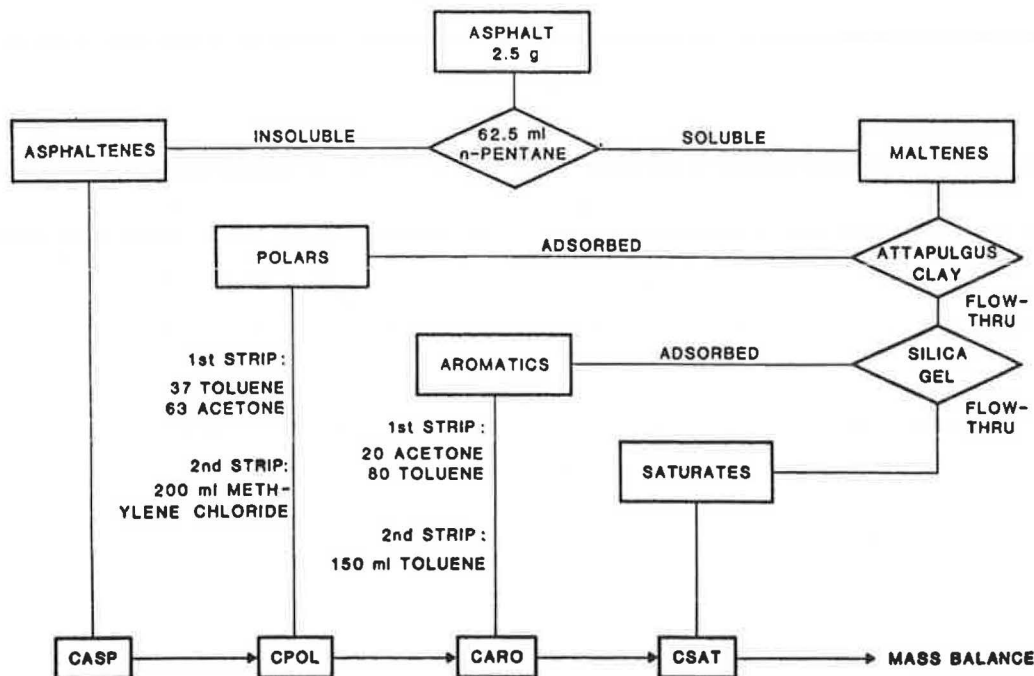Variables for the analysis were

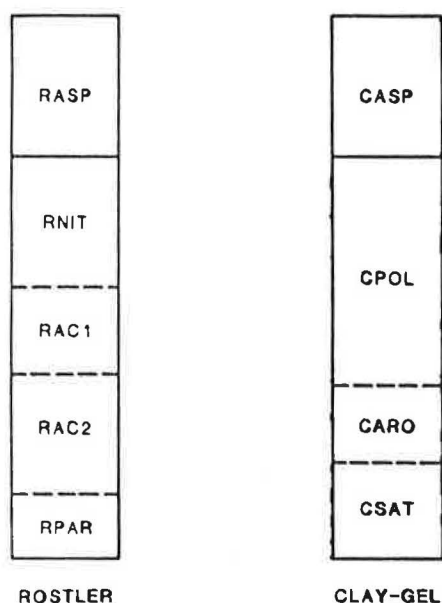FIGURE 2 Schematic, clay-gel separation.

FIGURE 3 Comparison of fractional composition by Rostler and clay-gel separations.

Rostler Components

- RASP = Rostler asphaltenes,
- RNIT = Rostler nitrogen bases,
- RAC1 = Rostler first acidaffins,
- RAC2 = Rostler second acidaffins, and
- RPAR = Rostler paraffins.

Clay-Gel Components

- CASP = Clay-gel asphaltenes,
- CPOL = Clay-gel polars,
- CARO = Clay-gel aromatics, and
- CSAT = Clay-gel saturates.

Relationships studied were of the following general linear forms:

$$CASP = X_1(RASP) + z_1$$

$$CPOL = X_2(RNIT) + X_3(RAC1) + X_4(RAC2) + X_5(RPAR) + z_2$$

$$CARO = X_6(RNIT) + X_7(RAC1) + X_8(RAC2) + X_9(RPAR) + z_3$$

$$CSAT = X_{10}(RNIT) + X_{11}(RAC1) + X_{12}(RAC2) + X_{13}(RPAR) + z_4$$

where X_i is regression coefficients and z_i is intercepts.

After all combinations of regressions were run to include from one to four Rostler components for each predicted clay-gel component (372 combinations of four equations for 31 materials), equation forms and correlation coefficients were studied to select what appeared to be the most logical candidates for a practical relationship. After regression equations were chosen, average unit error (measured composition - predicted composition) and relative error [(unit error/measured composition) x 100] were calculated.

Table 1 gives measured Rostler and clay-gel composition for the materials used in this study.

RESULTS

Table 2 gives regression coefficients for all data. After a subjective review of the regression coefficients, correlation coefficients, and component balances (Table 3), the following relationships were selected for further study:

$$CASP = 0.980(RASP) + 0.728 \qquad (R^2 = 0.99)$$

$$CSAT = 0.964(RPAR) + 2.314 \qquad (R^2 = 0.98)$$

$$CPOL = 0.773(RNIT) + 0.971(RAC1) - 0.632(RAC2) + 21.619 \qquad (R^2 = 0.89)$$

$$CARO = 0.153(RNIT) - 0.069(RAC1) + 1.661(RAC2) - 21.394 \qquad (R^2 = 0.92)$$

TABLE 1 Measured Composition

Material	RASP	RNIT	RAC1	RAC2	RPAR	CASP	CPOL	CARO	CSAT
LorCon	26.3	24.4	15.9	22.0	11.4	27.6	42.3	14.3	15.7
PopCon	38.9	17.9	13.3	19.7	9.6	37.7	36.2	15.7	11.8
MBD-11	32.1	14.7	10.8	19.7	22.7	32.9	29.7	15.1	20.9
MBD-12	22.9	20.9	13.2	22.7	20.3	23.1	38.0	13.8	25.1
MBD-21	26.3	17.4	17.6	25.7	13.0	26.6	41.4	16.8	14.8
MBD-31	28.0	25.5	14.8	20.7	11.0	26.1	48.2	14.3	11.4
MBD-41	34.7	16.2	12.4	21.9	14.8	35.9	33.4	17.6	13.3
MBD-42	23.7	23.2	15.4	24.1	13.6	24.9	39.9	16.6	18.7
MBD-51	33.6	19.0	13.8	21.9	11.7	33.8	36.8	17.0	12.3
MBD-52	20.8	24.6	15.8	26.3	12.5	22.4	41.4	18.4	17.8
MBD-91	33.1	18.3	16.5	22.4	9.7	32.7	39.9	17.0	10.1
MBD-01	0	0	0.1	15.2	84.7	0.2	2.7	12.7	84.3
MBD-02	19.6	17.4	19.5	28.5	15.0	20.4	35.5	23.2	20.8
MBD-2B	18.6	23.9	19.4	24.9	13.2	21.8	35.1	24.9	17.7
MBD-03	9.0	38.9	14.9	23.2	14.0	9.8	49.9	24.3	16.0
MBD-04	0	2.3	4.3	41.5	51.9	0.7	5.0	44.0	50.5
MBD-05	0.4	22.0	16.7	38.2	22.7	0.2	27.7	49.0	23.5
MBD-6A	23.1	20.4	18.4	24.1	14.0	23.8	34.6	26.4	15.2
MBD-6B	7.9	33.4	13.3	25.3	20.1	8.5	43.1	27.0	21.4
MBD-7A	0	9.3	19.1	52.3	19.3	0.2	15.6	62.4	22.2
MBD-8A	0	8.7	24.1	52.3	14.7	0.3	22.0	60.2	17.8
MBD-09	0	22.9	24.6	44.9	7.6	0.1	29.1	64.5	6.4
MBD-9R	0	22.9	24.2	45.3	7.6	0.1	29.1	54.5	6.4
MBD-92	21.1	25.3	17.2	25.8	10.6	22.2	41.5	24.4	11.8
MBD-2B2	20.6	24.0	17.9	25.1	12.4	21.9	41.6	24.1	12.4
MBD-6A1	30.6	20.2	16.4	21.2	11.6	30.3	42.6	15.9	11.1
MBD-6B2	19.0	28.9	13.6	23.3	15.2	19.0	44.2	18.7	18.2
MBD-7A1	34.0	16.5	14.2	23.8	11.5	32.0	34.8	21.3	11.9
MBD-7A2	21.4	22.6	15.8	27.7	12.5	22.0	39.1	21.9	17.0
MBD-8A1	33.3	16.8	15.3	24.2	10.4	30.8	36.3	22.3	10.6
MBD-8A2	20.9	23.0	16.5	28.2	11.4	22.3	39.8	21.8	16.1

TABLE 2 Regression Coefficients, All Data

Run	Dependent	RASP	RNIT	RAC1	RAC2	RPAR	Intercept	R^2
1	CASP	0.980	0	0	0	0	0.728	0.99
2	CSAT	0	0	0	0	0.964	2.314	0.98
3	CSAT	0	0	0	−0.013	0.964	2.675	0.98
4	CSAT	0	0	0.172	−0.053	1.005	0.395	0.98
5	CSAT	0	0.054	0.157	−0.037	1.020	−1.168	0.98
6	CPOL	0	1.196	0	0	0	10.760	0.74
7	CPOL	0	1.176	0.084	0	0	9.845	0.74
8	CPOL	0	0.773	0.971	−0.632	0	21.619	0.89
9	CPOL	0	0.619	0.023	−0.455	−0.366	40.870	0.94
10	CARO	0	−0.374	0	0	0	34.271	0.03
11	CARO	0	−0.905	2.260	0	0	9.524	0.44
12	CARO	0	0.153	−0.069	1.661	0	−21.394	0.92
13	CARO	0	0.273	0.672	1.522	0.286	−36.449	0.94

TABLE 3 Component Balance Based on Regression Coefficients

Set	RASP	RNIT	RAC1	RAC2	RPAR
1	98.0	NA	NA	NA	NA
2	NA	0	0	0	96.4
9	NA	61.9	2.3	−45.5	−36.6
13	NA	27.3	67.2	152.2	28.6
Σ		89.2	69.5	106.7	88.4
2	NA	0	0	0	96.4
8	NA	77.3	97.1	−63.2	0
13	NA	27.2	67.2	152.2	28.6
Σ		104.6	164.3	89.0	125.0
2	NA	0	0	0	96.4
8	NA	77.3	97.1	−63.2	0
12	NA	15.3	−6.9	166.1	0
Σ		92.6	90.2	102.9	96.4

Note: Combination 1-2-8-12 used for this paper.

DISCUSSION

Correlation coefficients $[R = (R^2)^{1/2}]$ appear respectable and a review of the equations appears to support the hypothesis that some "compatibility" between components as measured by the two methods occurs. That is, clay-gel saturates consist mostly of Rostler paraffins, and clay-gel polars consist mostly of Rostler nitrogen bases. However, the analysis suggests that clay-gel aromatics consist primarily of Rostler second acidaffins with some nitrogen bases.

Physical significance of negative regression coefficients in the relationships for clay-gel polars and aromatics has not been determined at this time.

Component balance based on the predictive equations (calculations of total weight of the predicted component for a unit weight of the reference components, Rostler fractions) shows good balance for the predicted clay-gel asphaltenes and saturates (98.0 and 96.4 percent). Balance for clay-gel polars is 111.2 percent, and for aromatics the calculated balance is 174.5 percent, which may be cause for some concern and will be addressed later.

Table 4 gives predicted versus measured values (residuals) of each component for each material tested.

For recycle applications, some consider a minimum ratio of clay-gel polars to saturates as necessary for acceptable combinations of aged asphalt and recycle agents. Table 5 gives measured versus predicted ratios with unit and relative errors.

One measure of the usefulness of any fractional compositional method is the ability to predict composition of blends of materials when composition and concentration of each component are known. In other words, the measured composition of the blend should be close to the value calculated from the composition and concentrations of the components. Table 6 gives measured versus predicted composition of 15 blends of aged asphalt and recycle agents. Seventy-one percent of the predictions are within 2 percent (unit error) of the measured values, which would suggest, in view of normal testing repeatability, that the modified clay-gel method, as used for this study, is sound.

CONCLUSIONS

On the basis of the materials used for this study, it appears that reasonable predictions of clay-gel composition of asphalt can be made from data on Rostler composition. Within the constraints of this study, it should be possible to use the data bank of information on FHWA asphalts and performance of these materials for studies on compositional effects of asphalt on performance for most purposes. The modified clay-gel method appears to be capable of reasonably predicting composition of blends of two materials (i.e., theoretical fractional composition of blends is practically the same as measured composition).

MODIFIED CLAY-GEL METHOD

This method is a modification of ASTM Standard Method D 2007, "Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatagraphic Method."

This section will show changes or modifications of the referenced ASTM Standard Method.

Sample Preparation

1. Weigh 2.5 ± 0.5 g sample to the nearest 0.5 mg in a 250-mL conical flask.
2. Add 25 mL pentane per gram of sample.
3. Heat in a warm water bath for a few seconds with swirling.
4. Let stand overnight at room temperature in a covered flask.

Collection of Asphaltenes

1. Weigh 150-mL capacity Buchner funnel with a fine fritted glass filter and attach to a 500-mL filtering flask attached to an aspirator.
2. Filter the sample through the funnel using care not to allow filtrate to be drawn into the vacuum line.
3. Rinse the 250-mL conical flask twice with 20 mL pentane and pour through the funnel.

4. Wash approximately 1500 mL pentane through the funnel to remove all of the maltenes from the asphaltenes. The amount of pentane required may vary, depending on the asphalt. Use adequate pentane until the filtrate is clear. If it is necessary to remove some of the filtrate from the receiving flask, empty the flask into a 100-mL round bottom flask and remove excess solvent with a rotary evaporator. This evaporation should continue until the filtrate is reduced in volume to about 35 to 50 mL of maltenes plus solvent.

5. Aspirate the precipitate in the funnel for a maximum of 45 min. Wipe the funnel dry and weight it.

6. Determine the amount of asphaltenes by subtracting the tare weight of the funnel.

TABLE 4   Measured Versus Predicted Composition

Material	Asphaltenes		Polars		Aromatics		Saturates	
	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
LorCon	27.6	26.5	42.3	42.0	14.3	17.8	15.7	13.3
PopCon	37.7	38.8	36.2	36.5	15.7	13.1	11.8	11.6
MBD-11	32.9	32.2	29.7	31.0	15.1	12.8	20.9	24.2
MBD-12	23.1	23.2	38.0	36.2	13.8	18.6	25.1	21.9
MBD-21	26.6	26.5	41.5	35.9	16.8	22.7	14.8	14.8
MBD-31	26.1	28.2	48.2	42.6	14.3	15.9	11.4	12.9
MBD-41	35.9	34.7	33.4	32.3	17.6	16.6	13.3	16.6
MBD-42	24.9	24.0	39.9	39.3	16.6	21.1	18.7	15.4
MBD-51	33.8	33.7	36.8	35.9	17.0	16.9	12.3	13.6
MBD-52	22.4	21.1	41.4	39.4	18.4	25.0	17.8	14.4
MBD-91	32.7	33.2	39.9	37.6	17.0	17.5	10.1	11.7
MBD-01	0.2	0.7	2.7	12.1	12.7	3.8	84.3	84.0
MBD-02	20.4	19.9	35.5	36.0	23.2	27.3	20.8	16.8
MBD-2B	21.8	19.0	35.1	43.2	24.9	22.3	17.7	15.0
MBD-03	9.8	9.5	49.9	51.5	24.3	22.1	16.0	15.8
MBD-04	0.7	0.7	5.0	1.3	44.0	47.6	50.5	52.3
MBD-05	0.2	1.1	27.7	30.7	49.0	44.3	23.5	24.2
MBD-6A	23.8	23.4	34.6	40.0	26.4	20.5	15.2	15.8
MBD-6B	8.5	8.5	43.1	44.4	27.0	24.8	21.4	21.7
MBD-7A	0.2	0.7	15.6	14.3	62.4	65.6	22.2	20.9
MBD-8A	0.3	0.7	22.0	18.7	60.2	65.1	17.8	16.5
MBD-09	0.1	0.7	29.1	34.8	64.5	55.0	6.4	9.6
MBD-9R	0.1	0.7	29.1	34.2	64.5	55.7	6.4	9.6
MBD-92	22.2	21.4	41.5	41.6	24.4	24.1	11.8	12.5
MBD-2B2	21.9	20.9	41.6	41.7	24.1	22.7	12.4	14.3
MBD-6A1	30.3	30.7	42.6	39.8	15.9	15.8	11.1	13.5
MBD-6B2	19.0	19.3	44.2	42.4	18.7	20.8	18.2	17.0
MBD-7A1	32.0	34.0	34.8	33.1	21.3	19.7	11.9	13.4
MBD-7A2	22.0	21.7	39.1	36.9	21.9	27.0	17.0	15.5
MBD-8A1	30.8	33.4	36.3	34.2	22.3	20.3	10.6	12.3
MBD-8A2	22.3	21.2	39.8	37.6	21.8	27.8	16.1	13.3

TABLE 5   Measured Versus Predicted Polars to Saturates (P/S)

Material	Measured			Predicted			Error	
	P	S	P/S	P	S	P/S	Unit	Relative
LorCon	42.3	15.7	2.69	42.0	15.7	2.68	0.01	0.37
PopCon	36.2	11.8	3.07	36.5	11.6	3.15	-0.08	-2.61
MBD-11	29.7	20.9	1.42	31.0	24.2	1.28	0.14	9.86
MBD-12	38.0	25.1	1.51	36.2	21.9	1.65	-0.14	-9.18
MBD-21	38.0	14.8	2.80	35.9	14.8	2.43	0.38	13.49
MBD-31	48.2	11.4	4.23	42.6	12.9	3.30	0.93	21.90
MBD-41	33.4	13.3	2.51	32.3	16.6	1.95	0.57	22.52
MBD-42	39.9	18.7	2.13	39.3	15.4	2.55	-0.42	-19.60
MBD-51	36.8	12.3	2.99	35.8	13.6	2.63	0.36	12.02
MBD-52	41.4	17.8	2.33	39.3	14.4	2.73	-0.40	-17.34
MBD-91	39.9	10.1	3.95	37.6	11.7	3.21	0.74	18.65
MBD-01	2.7	84.3	0.03	12.1	83.9	0.14	-0.11	-350.28
MBD-02	35.5	20.8	1.71	36.0	16.8	2.14	-0.44	-25.55
MBD-2B	35.1	17.7	1.98	43.2	15.0	2.88	-0.90	-45.23
MBD-03	49.9	16.0	3.12	51.5	15.8	3.26	-0.14	-4.51
MBD-04	5.0	50.5	0.09	1.3	52.3	0.02	0.07	74.89
MBD-05	27.7	23.5	1.18	30.7	24.2	1.27	-0.09	-7.62
MBD-6A	34.6	15.2	2.28	40.0	15.8	2.53	-0.26	-11.22
MBD-6B	43.1	21.4	2.01	44.3	21.7	2.04	-0.03	-1.36
MBD-7A	15.6	22.2	0.70	14.3	20.9	0.68	0.02	2.63
MBD-8A	22.0	17.8	1.24	18.7	16.5	1.13	0.10	8.30
MBD-09	29.1	6.4	4.55	34.8	9.6	3.62	0.92	20.27
MBD-9R	29.1	6.4	4.55	34.2	9.6	3.56	0.98	21.65
MBD-92	41.5	11.8	3.52	41.5	12.5	3.32	0.20	5.60
MBD-2B2	41.6	12.4	3.35	41.7	14.3	2.92	0.44	13.08
MBD-6A1	42.6	11.1	3.84	39.7	13.5	2.94	0.90	23.38
MBD-6B2	44.2	18.2	2.43	42.4	17.0	2.49	-0.07	-2.70
MBD-7A1	34.8	11.9	2.92	33.1	16.4	2.02	0.91	30.98
MBD-7A2	39.1	17.0	2.30	36.9	14.4	2.56	-0.26	-11.41
MBD-8A1	36.3	10.6	3.42	34.1	12.3	2.77	0.65	19.04
MBD-8A2	39.8	16.1	2.47	37.6	13.3	2.83	-0.36	-14.36

TABLE 6 Measured Versus Calculated Blend Components

Blend	MBD-11	MBD-12	MBD-21	MBD-31	MBD-41
Asphalt	PopCon	LorCon	PopCon	PopCon	PopCon
Modifier	MBD-01	MBD-01	MBD-02	MBD-03	MBD-04
Asphalt (%)	84	87.5	35	64	90
CASP in asphalt (%)	37.7	27.6	37.37	37.7	37.7
CASP in modifier (%)	0.2	0.2	20.4	9.8	0.7
Measured CASP in blend	32.9	23.1	26.6	26.1	35.9
Calculated CASP in blend	31.2	24.2	26.5	27.7	34.0
Unit CASP error	1.2	−1.1	0.1	−1.6	1.9
Relative CASP error (%)	3.6	−4.7	0.5	−6.0	5.3
CPOL in asphalt (%)	36.2	42.3	36.2	36.2	36.2
CPOL in modifier (%)	2.7	2.7	35.5	49.9	5.0
Measured CPOL in blend	29.7	38.0	41.5	48.2	33.4
Calculated CPOL in blend	30.8	37.3	35.7	41.1	33.1
Unit CPOL error	−1.1	0.6	5.8	7.1	0.3
Relative CPOL error (%)	−3.8	1.7	13.9	14.7	9.6
CARO in asphalt (%)	15.7	14.3	15.7	15.7	15.7
CARO in modifier (%)	12.7	12.7	23.2	24.3	44.0
Measured CARO in blend	15.1	13.8	16.8	14.3	17.6
Calculated CARO in blend	15.2	14.1	20.6	18.8	18.5
Unit CARO error	−0.1	−0.3	−3.8	−4.5	−0.9
Relative CARO error (%)	−0.8	−2.2	−22.5	−31.4	−5.3
CSAT in asphalt (%)	11.8	15.7	11.8	11.8	11.8
CSAT in modifier (%)	84.3	84.3	20.8	16.0	50.5
Measured CSAT in blend	20.9	25.1	14.8	11.4	13.3
Calculated CSAT in blend	23.4	24.3	17.7	13.3	15.7
Unit CSAT error	−2.5	0.8	−2.9	−1.9	−2.4
Relative CSAT error (%)	−12.0	3.3	−19.2	−16.8	−17.8
Average unit error	−0.62	0.00	−0.20	0.23	−0.28
Average relative error	−3.25	−0.48	−6.85	−9.88	−2.05
CASP in asphalt (%)	27.6	37.37	27.6	37.7	27.6
CASP in modifier (%)	0.7	0.2	0.2	0.1	0.1
Measured CASP in blend	35.9	33.8	22.4	32.7	22.2
Calculated CASP in blend	25.2	32.8	22.3	33.2	22.7
Unit CASP error	10.7	1.0	0.1	−0.5	−0.5
Relative CASP error (%)	29.9	2.9	6.4	−1.5	−2.0
CPOL in asphalt (%)	42.3	36.2	42.3	36.2	42.3
CPOL in modifier (%)	5.0	27.7	27.7	29.1	29.1
Measured CPOL in blend	33.4	36.8	41.4	39.9	41.5
Calculated CPOL in blend	38.9	35.1	39.5	35.3	39.9
Unit CPOL error	−5.5	1.7	1.9	4.6	1.6
Relative CPOL error (%)	−16.6	4.6	4.7	11.4	3.8
CARO in asphalt (%)	14.3	15.7	14.3	15.7	14.3
CARO in modifier (%)	44.0	49.0	49.0	15.7	64.5
Measured CARO in blend	17.6	17.0	18.4	17.0	24.4
Calculated CARO in blend	17.0	20.0	21.1	21.6	23.3
Unit CARO error	0.6	−3.0	−2.7	−4.6	1.1
Relative CARO error (%)	3.6	−17.8	−14.5	−26.8	4.4
CSAT in asphalt (%)	15.7	11.8	15.7	11.8	15.7
CSAT in modifier (%)	50.5	23.5	23.5	6.4	6.4
Measured CSAT in blend	13.3	12.3	17.8	10.1	11.8
Calculated CSAT in blend	18.8	13.3	17.2	11.2	14.0
Unit CSAT error	−5.5	−1.0	0.6	−1.1	−2.2
Relative CSAT error (%)	−41.6	−8.3	3.3	−10.4	−18.9
Average unit error	0.08	−0.33	0.03	−0.40	0.00
Average relative error	−6.18	−4.65	−0.03	−6.83	−3.18
CASP in asphalt (%)	27.6	37.7	27.6	37.7	27.6
CASP in modifier (%)	21.8	28.3	8.5	0.2	0.2
Measured CASP in blend	21.9	30.3	19.0	32.8	22.0
Calculated CASP in blend	22.9	33.7	19.0	32.8	22.9
Unit CASP error	−1.0	−3.4	0.0	0.8	0.9
Relative CASP error (%)	−4.4	−11.1	−2.6	−2.6	−4.3
CPOL in asphalt (%)	42.3	36.2	42.3	36.2	42.3
CPOL in modifier (%)	35.1	34.6	43.1	15.6	15.6
Measured CPOL in blend	41.6	42.6	44.2	34.8	39.1
Calculated CPOL in blend	36.4	35.5	42.7	33.5	37.8
Unit CPOL error	5.2	7.1	1.5	1.3	1.3
Relative CPOL error (%)	12.4	16.6	3.5	3.7	3.4
CARO in asphalt (%)	14.3	15.7	14.3	15.7	14.3
CARO in modifier (%)	24.9	26.4	27.0	62.4	62.4
Measured CARO in blend	24.1	15.9	18.7	21.3	21.9
Calculated CARO in blend	22.9	20.3	20.0	21.8	22.5
Unit CARO error	1.2	−4.4	−1.3	−0.5	−0.6
Relative CARO error (%)	4.8	−27.7	−7.0	−2.2	−2.6
CSAT in asphalt (%)	15.7	11.8	15.7	11.8	15.7
CSAT in modifier (%)	17.7	15.2	21.41	22.2	22.2
Measured CSAT in blend	12.4	11.1	18.2	11.9	17.0
Calculated CSAT in blend	17.3	13.3	18.3	13.2	16.8
Unit CSAT error	−0.1	−1.3	0.2	−2.2	0.0
Relative CSAT error (%)	−39.8	−19.5	−3.6	−10.5	1.1
Average unit error	0.13	−0.73	0.03	−0.33	0.0
Average relative error	−6.75	−10.43	−2.43	−2.90	−0.60

Fractionation

1. Place 100 g of Attapulgus clay in upper section of column in three increments. At each increment, gently tap the sides of the column with a rubber stopper on the end of a glass rod to obtain uniform packing.
2. Place 200 g of silica gel plus 50 g of clay on top of the gel in the lower section of the column in incremental amounts and tap the sides as stated in Step 1.
3. Place a plug of glass wool over the top surface of the upper column.
4. Join the columns with a No. 4 stopper.
5. Add 25 mL pentane to the upper column and allow to percolate into the clay.
6. When nearly all the pentane has entered the column, add the maltene filtrate obtained as per "Collection of Asphaltenes." This can be accomplished by use of a 65-mm-diameter wide-stem funnel. Keep the funnel on top of the column and do not allow air to enter the clay bed.
7. Wash the flask with pentane and add washings to the column.
8. Wash the walls of the column with pentane when nearly all the previous material has entered the clay.
9. Wash the sample flask again and add washings to the column.
10. Wash walls of column again.
11. When nearly all the washings have entered the clay, add pentane to the column and maintain head well above the clay bed.
12. Collect 250 mL of the first pentane effluent in a preweighed 500-mL widemouthed conical flask.
13. Disconnect the two column sections and continue washing the upper clay section with pentane.
14. Maintain a moderate liquid head level above the clay during wash and adjust pentane additions to ensure the liquid head level is about 25 mm when 150 mL has been collected.
15. Stop adding pentane and allow the liquid to drain from column. There should be ±250 mL in the second receiver flask. Save this fraction because it is part of the aromatics fraction.
16. Add 37 percent toluene/63 percent acetone to the Attapulgus clay and collect the effluent. Usually about 1000 to 1500 mL is required to wash until the effluent is clear. This effluent contains the polar fraction.
17. Add 200 mL methylene chloride to the clay column for the final stripping of any polars that remain adsorbed to the clay.
18. Add 1500 mL 80 percent toluene/20 percent acetone through the silica column to strip off the aromatic fraction. Combine with the aromatic fraction collected from the clay column in Step 15.
19. Add 100 to 200 mL pure toluene to the silica gel column for the final strip and add to the aromatic fraction.

Solvent Removal

1. Transfer the effluents for each of the three fractions (saturates, aromatics, and polars) to 1000-mL round flasks and place in a rotary evaporator equipped with an N_2 sweep. Evaporate the solvent until not more than 20 to 30 mL of solvent plus sample fraction remains. Transfer to preweighed 500-mL conical flasks. Rinse the round bottom flasks with pentane and place these rinses in the respective conical flasks.
2. Evaporate the last of the solvent from the conical flasks over a water bath with an N_2 jet 15 to 25 mm above the liquid.
3. When the solvent is evaporated, remove one flask at a time and place on a hot plate at 260°C (500°F) and continue the N_2 sweep.
4. Remove the flask from the hot plate when the first trace of smoke appears at the top of the flask.
5. Continue agitation of the surface of the sample with the N_2 jet for about 30 sec and then return the flask to the hot plate.
6. Repeat the sequence.
7. After the solvent is removed, wipe the outside with a clean cloth and cool to room temperature.
8. Weigh and determine the amount of residue by subtracting the tare weight of the flask.

Calculations

Percentage asphaltenes = (B/A) x 100

Percentage saturates = (C/A) x 100

Percentage aromatics = (D/A) x 100

Percentage polars = (E/A) x 100

where

A = grams of original sample used;
B = grams of precipitate in Buchner funnel (asphaltenes);
C = grams of residue from pentane effluent (saturates);
D = grams of residue collected in Steps 15, 18, and 19 (aromatics); and
E = grams of residue collected in Steps 16 and 17 (polars).

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