PB82196239

HIGHWAY BINDER MATERIALS FROM MODIFIED SULFUR-WATER EMULSIONS

APRIL 1982

FINAL REPORT

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Federal Highway Administration Offices of Research and Development Materials Division Washington, D. C. 20590

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Technical Report Documentation Page

1. Report No.	2. Government Acces	sion No. 3	, Recipient's Catalog (10.	
FHWA/RD-82/035			PB32 196	239	
4. Title and Subtitle			Report Date		
Highway Binder Materia		April, 1982			
Modified Sulfur-Water	Emulsions	6	Performing Organizati 2390.T031	on Code	
7. Author(s)			Petforming Ocennizati	an Report No.	
J. C. Rosner and J. G.					
9. Performing Organization Name and Addres	5	1	Work Unit No.		
Engineers Testing Labou	atories. In	c.	FCP 34G1-14	2	
3737 East Broadway Road	1 1	1	1. Contract or Grant No	3.	
Phoenix, Arizona 85030	5		DOT-FH-11-9664		
		1	1. Type of Report and I	Period Covered	
12. Sponsoring Agency Name and Address			Final		
U. S. Department of Tra	insportation		rinal		
Federal Highway Adminis	stration	-	[
Washington, D. C. 2059	90		M/0758	.00*	
15. Supplementary Notes		l			
FHWA Contract Manager.	Brian H. C	hollar HRS-23			
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16. Abstract					
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17. Key Hords	<u> </u>	18. Distribution Stateme			
Sulfur-extended-asphal Sulphlex, emulsions, asphalt, distillation, tall oil, emulsifiers	t,	No original dis agency. This d public only thr Information Ser Virginia 22161	tribution by th ocument is ava- ough the Nation vice, Springfic	ne sponsoring ilable to the nal Technical eld,	
19. Security Classel. (of this report)	20. Security Clas	sit. (of this page)	21. No. of Pages	22. Price	
Unclassified	Unclassif	ied	137		
Form DOT F 1700.7 (8-72)				I	

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INDEX

	PAGE NO.
TECHNICAL REPORT DOCUMENTATION PAGE	. i
INDEX	. ii-iii
LIST OF FIGURES	iv-v
LIST OF TABLES	. vi-viii
<pre>1.0 INTRODUCTION</pre>	1 1 2 2
2.0 SULFUR-EXTENDED-ASPHALT AND SULPHLEX BASE STOCKS USED IN EMULSION FORMULATION	. 3 . 3
 3.0 EMULSION FORMULATION AND PRODUCTION	8 8 8 12 13
4.0 PHYSICAL CHARACTERISTICS OF SULFUR-EXTENDED- ASPHALT AND SULPHLEX EMULSIONS	14 14 16 16 18 19 19 23 23 23 24 25 27

5.0 5.1 5.2 5.3	PHYSICAL CHARACTERISTICS OF SULFUR-EXTENDED-ASPHALT AND SULPHLEX EMULSION RESIDUES1Data Analyses2Residue From Distillation3Residue From Evaporation	30 30 30 32
6.0	COMPARISON OF PROPERTIES OF SULFUR-EXTENDED- ASPHALT AND SULPHLEX EMULSIONS TO ASTM D977 AND D2397 REQUIREMENTS	35
7.0	CONCLUSIONS	41
8.0	RECOMMENDATIONS FOR FUTURE RESEARCH	42
	REFERENCES	43
·	APPENDIX A - Emulsion Formulation Research by Robert L. Dunning	45
	APPENDIX B - Modified Distillation Procedure	106
	APPENDIX C - Physical Properties of Emulsions .	110
	APPENDIX D - Physical Properties of Emulsion Residues by Distillation and Evaporation	123

÷

.

LIST OF FIGURES

Figure <u>No.</u>		Page No.
1	Emulsion Formulation Experiment Matrix	9
2	Experimental Analysis Matrix	15
3	Storage Stability versus Percent Sulfur in Binder	20
4	Water Miscibility of Sulfur-Water Emulsions	26
5	Comparison of Residue Contents by Distillation and Evaporation	26
6	Demulsibility of Anionic Rapid Set Emulsions	28
7	Penetration at 77F (25C) of SS and RS Emulsions .	31
8	Ductility at 77F (25C) of Distillation Residues .	33
9	Penetration at 77F (25C) of Evaporation Residues	33
10	Schematic Diagram of Modified Distillation Apparatus	109
11	Newman-Keuls Ranking, Water Content by Distillation	111
12	Newman-Keuls Ranking, Water Content by Evaporation	112
13	Newman-Keuls Ranking, Storage Stability	113
14	Newman-Keuls Ranking, Emulsion Break Time	115
15	Newman-Keuls Ranking, Saybolt Furol Viscosity	116
16	Newman-Keuls Ranking, Water Miscibility	118

17	Newman-Keuls Ranking, Residue Content by Distillation	119
18	Newman-Keuls Ranking, Residue Content by Evaporation	120
19	Newman-Keuls Ranking, Demulsibility	121
20	Newman-Keuls Ranking, Penetration of Distillation Residue	124
21	Newman-Keuls Ranking, Absolute Viscosity of Distillation Residue	125
22	Newman-Keuls Ranking, Ductility of Distillation Residue	126
23	Newman-Keuls Ranking, Penetration of Evaporation Residue	127
24	Newman-Keuls Ranking, Absolute Viscosity of Evaporation Residue	128
25	Newman-Keuls Ranking, Ductility of Evaporation Residue	129

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LIST OF TABLES

Table No.		Page No.
1	Absolute Viscosity and Penetration of U.S. Oil and Refining AR2000 at Sulfur Extensions of 0, 10, 15, 30, and 50 Percent	4
2	Formulations of Sulphlex Samples	5
3	Penetration and Absolute Viscosity of Unaged and RTFOT Aged Sulphlex Samples	7
4	Emulsifiers Which Were Studied During Formulation Experiments	10
5	Emulsion Designations and Formulations Which Were Characterized	1 7
6	Gradation, Specific Gravity, and Absorption of Graniterock Aggregate Used in Emulsion Break Time Determinations	21
7	Specific Gravities of Emulsions and Residues	22
8	Comparison of Anionic Slow Set SEA Emulsion Properties to Several ASTM D977 Requirements for SS-1 Emulsions	36
9	Comparison of Anionic Rapid Set SEA and Sulphlex Emulsion Properties to Several ASTM D977 Requirements for RS-1 Emulsions	37
10	Comparison of Cationic Slow Set SEA Emulsion Properties to ASTM D2397 Requirements for CSS-1 Emulsions	38
11	Comparison of Cationic Rapid Set SEA Emulsion Properties to ASTM D2397 Requirements for CRS-1 Emulsions	40

12	Water Content by Distillation; %	111
13	One-Way ANOVA Summary, Water Content by Distillation	111
14	Water Content by Evaporation; %	112
15	One-Way ANOVA Summary, Water Content by Evaporation	112
16	Storage Stability; %	113
17	One-Way ANOVA Summary, Storage Stability	113
18	Freeze-Thaw Resistance	114
19	Emulsion Break Time; min	115
20	One-Way ANOVA Summary, Emulsion Break Time	115
21	Saybolt Furol Viscosity, 77F; sec	116
22	One-Way ANOVA Summary, Saybolt Furol Viscosity	116
23	Coating Ability of Sulfur Water Emulsions	1 17
24	Water Miscibility, Maximum Difference; %	118
25	One-Way ANOVA Summary, Water Miscibility	118
26	Residue Content by Distillation; %	119
27	One-Way ANOVA Summary, Residue Content by Distillation	119
28	Residue Content by Evaporation; %	120
29	One-Way ANOVA Summary, Residue Content by Evaporation	120
30	Demulsibility; %	121
31	One-Way ANOVA Summary, Demulsibility	121
32	Long Term Stability of SEA and Sulphlex Emulsions	122

,

vii

33	Penetration of Residue From Distillation, 77F, 100g; 1/10 mm 124
34	One-Way ANOVA Summary, Penetration of Distillation Residue 124
35	Absolute Viscosity of Residue From Distillation, 140F; Poise
36	One-Way ANOVA Summary, Absolute Viscosity of Distillation Residue 125
37	Ductility of Residue From Distillation 77F, 5 cm/min; cm 126
38	One-Way ANOVA Summary, Ductility of Distillation Residue
39	Penetration of Residue From Evaporation 77F, 100g; 1/10 mm 127
40	One-Way ANOVA Summary, Penetration of Evaporation Residue
41	Absolute Viscosity of Residue From Evaporation, 140F; Poise 128
42	One-Way ANOVA Summary, Absolute Viscosity of Evaporation Residue 128
43	Ductility of Residue From Evaporation, 77F, 5 cm/min; cm 129
44	One-Way ANOVA Summary, Ductility of Evaporation Residue

viii

1.0 INTRODUCTION

1.1 Background

During the past decade, the cost of asphalt cement has increased drastically and at times and in certain locations, the supply has been unpredictable. In order to lessen the dependence of the highway industry on asphalt cement, extensive research with the objective of developing asphalt cement extenders or substitutes has and is currently being performed by various governmental and private agencies. Sulfur has been identified as a material which may have promise of being used as a partial replacement or substitute for asphalt cement. Also, sulfur is an attractive material for use in paving because of the predicted future surplus of the material resulting from increased involuntary production. Extensive laboratory (1*, 2, 3, 4, 5) and field (6, 7, 8, 9) research has been performed with sulfur-extendedasphalt materials. Most of this research has used elemental sulfur to extend the asphalt cement by up to 50 percent by weight. However, a problem which exists when constructing pavements using sulfurextended-asphalts is that during mixing and laydown, if mixture temperatures exceed approximately 300F (148.9C), sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) can be evolved creating possible health and environmental hazards.

A second method of using sulfur in pavement construction is using sulfur (in a modified form) as a total replacement for asphalt cement (10). The modification which has been studied consists of chemically modifying elemental sulfur to yield a material which, in many ways, is similar to asphalt cement. These modified (plasticized) sulfur materials will require much research in both the laboratory and in field applications to assess their true potential utility.

Asphalt emulsions (a fluid dispersion of asphalt and water) are commonly used in pavement construction and, in many instances, can be used in place of asphalt cements or cutback asphalts (13, 14). Asphalt emulsions can be mixed with aggregate and compacted at ambient temperatures.

*Note: Numbers in parenthesis refer to references listed on pages 43 to 44.

The major advantage of using asphalt emulsions over asphalt cements is that use of emulsions does not require mixture heating during production and thus, energy and cost savings can result. When emulsions are used in place of cutback asphalts, less hydrocarbons are lost to the atmosphere, resulting in less pollution and a savings in petroleum based solvents (15, 16).

The development and use of emulsified sulfurextended-asphalt and plasticized sulfur binders would be very advantageous. Mixing and compaction of paving mixtures containing the sulfur binders could be performed at ambient temperature resulting in reductions in health and environmental hazards from SO_2 and H_2S evolution and energy requirements due to ambient mixing temperature.

1.2 Project Objective

The objective of this project was to develop and characterize modified sulfur-water emulsions for use as highway binder materials.

1.3 Project Scope

Modified sulfur-water emulsions were produced with both sulfur-extended-asphalt (SEA) and plasticized sulfur (Sulphlex) materials using state-of-the-art knowledge of water emulsification systems and materials. Sulfur-extended-asphalt binders at four sulfur replacement levels - 10, 15, 30, and 40 percent and plasticized sulfur formulations were considered. Both cationic and anionic emulsions having slow, medium, and rapid setting characteristics containing both SEA and Sulphlex binders were studied. Successful emulsions which were produced were characterized using ASTM D244, "Standard Methods of Testing Emulsified Asphalts" (17) testing procedures and several non-standard procedures. 2.0 SULFUR-EXTENDED-ASPHALT AND SULPHLEX BASE STOCKS USED IN EMULSION FORMULATION

2.1 Sulfur-Extended Asphalt

Sulfur-extended-asphalts (SEA's) at four sulfur replacement percentages were emulsified. Replacement percentages used were 10, 15, 30, and 40 percent by weight of SEA binder.

Two asphalt base stocks were used during this project. An AR2000 from U.S. Oil and Refining of Tacoma, Washington was used for initial sulfur-extendedasphalt formulations. This asphalt was selected because experience has shown that it is of medium difficulty to emulsify. The second asphalt used was an AC-20 obtained from Husky Oil of Spokane, Washington.

Sulfur utilized in the SEA blends was obtained from U.S. Oil and Refining of Tacoma, Washington. The sulfur was a by-product of crude de-sulfurizing operations performed at the refinery.

For determining the physical characteristics of the sulfur-extended-asphalts, the SEA's were made by 'adding the sulfur in powdered form to the molten asphalt at 275F (135C) and mechanically mixing until uniform. Absolute viscosity results at 140F (60C) and penetration results at 77F (25C) for the U.S. Oil and Refining AR2000 and blends with 10, 15, 30, and 50 percent sulfur are tabulated in Table 1. From these results it is noted that sulfur additions decreased absolute viscosity and increased penetrations which indicate that the SEA's were softer than the unextended asphalt cement. Initial characterization experiments were performed with a maximum of 50 percent sulfur in the SEA binder, however, emulsion formulations with SEA binders used a maximum of 40 percent sulfur.

2.2 Sulphlex

This study was initially to emulsify four different Sulphlex formulations, however, most of the emulsification studies with Sulphlex were performed with one formulation. Samples of five different Sulphlex materials (Nos. 233, 233 CDC, 233 DPCD, 126, and 230) were obtained from Southwest Research Institute of San Antonio, Texas for experimentation. Formulations for these Sulphlexes are shown in Table 2.

ABSOLUTE VISCOSITY AND PENETRATION OF U.S. OIL AND REFINING AR2000 AT SULFUR EXTENSIONS OF 0, 10, 15, 30, and 50 PERCENT

	* S	ulfur (by	v weight	of Total	Mix)
Property	0	<u>10</u>	15	30	50
Absolute Viscosity, 140F, 30cm Hg; Poise	670.4	384.0	367.1	_*	_*
Penetration, 77F, 100g, 5 sec; 1/10 mm	133	1 82	216	226	186

*Note: At above 20 percent sulfur, sulfur separated from the asphalt and plugged viscometer tubes. No result could be obtained.

FORMULATIONS OF SULPHLEX SAMPLES

Sulp Desi	olex Ignation		Formulation
No.	233	70% Sulfur, 12%	CDC, 10% DP, 8% VT
No.	233 CDC	Same as No. 233 smaller batch	except supplied from a
No.	233 DCPD	70% Sulfur, 12%	DPCD, 10% DP, 8% VT
No.	126	61% Sulfur, 13%	CDC, 13% VT, 13% CT
No.	230	70% Sulfur, 15%	CDC, 15% DP

Note:	CDC	=	Cyclodiene Dimer Concentrate
	DP	=	Dipentene
	VT	=	Vinyl Toluene
	СТ	=	Coal Tar
	DPCD	=	Dicyclopentadiene

5

Absolute viscosity (ASTM D2171) and penetration (ASTM D5) tests were performed on the Sulphlex samples before and after aging in the rolling thin film oven in accordance with ASTM D2873. Results are tabulated in Table 3. Results show that penetrations, absolute viscosities, percent retained penetration, and viscosity aging index of the Sulphlex samples differed greatly. Unaged penetrations varied from 13 to 169 and aged penetrations from 8 to 74. Unaged viscosities varied from 106 to 2,999 poise and aged viscosities from 1,285 to 54,166 poise. Sulphlex 233 CDC was used for most of the emulsification experiments.

The three Sulphlex 233 formulations tested (233, 233 CDC, and 233 DPCD) were formulated and produced differently. The 233 Sulphlex was produced in a 7000 pound (3178 Kg) batch whereas the 233 CDC sample (which had the same formulation as the 233) was produced in a 500 pound (227 Kg) batch. The 233 DPCD was produced in a 500 pound (227 Kg) batch and contained dicyclopentadiene (DPCD) instead of cyclodiene dimer concentrate (CDC) as indicated in Table 2. The CDC utilized in the 233 and 233 CDC formulations was obtained from different batches from the same supplier.

PENETRATION AND ABSOLUTE VISCOSITY OF UNAGED AND RTFOT AGED SULPHLEX SAMPLES

		Penet: 100g;	cation; 7 1/10 mm	77F, (25C) Absolute	Absolute Viscosity, 140F (60C); Poise			
Sulphlex Designation		Unaged	RTFOT ¹ <u>Residue</u>	<pre>% Retained Penetration</pre>	Unaged	RTFOT ¹ Residue	Aging ² Index	
No. 23	3	139	8	6	966.1	54,166.2	56.1	
No. 23 CDC	3	169	74	44	106.0	1,285.4	12.1	
No. 23 DCPD	3	142	30	21	1055.1	13,920.0	13.2	
No. 12	6	13	9	69	_3	44,418.0	_3	
No. 23	0	82	41	50	2999.0	10,499.0	3.5	

Note:

¹ Residue from rolling thin film oven test.

2	Aging	Index	×	RTFOT Residue Viscosity
				Unaged Viscosity

³ Not determined

3.0 EMULSION FORMULATION AND PRODUCTION

3.1 Experimental Design

Emulsions were formulated and produced by Petroleum Sciences, Inc. Forty-eight different types of emulsions were to be formulated including both cationic and anionic emulsions with rapid, medium, and slow setting characteristics. Emulsions were to be formulated with four sulfur-extended-asphalts and four different Sulphlex formulations as base stocks. The emulsion formulation experiment matrix is shown in Figure 1.

Early in the project during formulation experiments, considerable difficulty was experienced with several of the formulations, especially with the cationics and emulsions which contained base stocks with a high specific gravity (sulfur-extended-asphalt at above 20 percent replacement and Sulphlex). Use of various combinations of emulsifiers was found to result in modified emulsion setting rates. For example, an emulsion which was formulated to be a slow set may actually have setting characteristics Therefore, modicloser to those of a medium set. fied sulfur water emulsions with only rapid and slow setting emulsifiers were studied. Additionally, only one Sulphlex formulation was used in emulsification experiments due to lack of sufficient supply and emulsification difficulties.

3.2 Emulsion Production

Details of emulsion production, methods, materials, experiments, and results are contained in Appendix A. Emulsions were prepared in the laboratory using two different types of mills - a modified centrifugal pump, and a Charlotte lab emulsion mill. During experimentation, it was found that superior emulsions of sulfur-extended-asphalts could be made if the sulfur and asphalt were pumped into the emulsion mill separately instead of simply combining a premixed sulfur-extended-asphalt with the soap phase in the mill. During the study, a wide variety of emulsifiers were used as tabulated in Table 4.



*Note: Signifies four different Sulphlex Formulations

FIGURE 1 Emulsion Formulation Experiment Matrix

9

EMULSIFIERS WHICH WERE STUDIED DURING FORMULATION EXPERIMENTS

Ingredient	Manufacturer	Type
Vinsol NVX and Resin	Hercules 1 Maritime Plaza Golden Gateway Center Suite 1250 San Francisco, CA. 94111 415-986-2535	Abdiatic acid. Anionic SS emulsifier
Orzan A	Crown Zellerbach Camas, Washington 206-834-4444	Sodium ligno sulfonate. dispersant for SS type emulsions.
Marasperse CE	American Can Company 908 Town & Country Blvd. Suite 230, Houston, Texas 77024	Sodium ligno sulfonate. dispersant for SS type emulsions.
SPV 200 Clay	American Colloid Company 5100 Suffield Court Skokie, Illinois	Bentonite clay
Natrosol 250HR	Hercules	Hydroxyethyl cellulcse viscosity builder.
Dresinate 731	Hercules	Anionic PS emulsifier. Rosin Soap
Pamak 4	Hercules	Anionic RS emulsifier, tall oil.
РАМАК 25	Hercules	Anicnic RS emulsifier, tall oil.
Pamak wifa	Hercules	Anionic RS emulsifier, tall oil.
Dresinate TX	Hercules	Anionic RS emulsifier, Rosin Scap.
NP 1007	Emery Industries 8733 S. Dice Rd. Santa Fe Springs, CA. 90670 213-723-8386	nonionic, CSS emulsifier, 100 mole ethoxylated nonyl phenol, 70%
Indulin W-3	Westvaco P.O. Box 5207 North Charleston, S.C. 29406 803-554-8350	Cationic, CSS emulsifier modified ligno sulforate.
TDA-40	Ettery	Nonionic, CSS emulsifier, 40 mole ethoxylated tri-

Arosurf AA-57

Sherex Chemical Company P.O. Box 646 Dublin, Chio 43017

decylalcohol. Cationic, CSS emulsifier,

amine

TABLE 4, continued

Ingredient	Manufacturer	Type	
Redicote E-11	Armak 8401 W. 47th St. McCock, Illionis 60525 313-242-2750	Cationic, CSS emulsifier amine	
Redicote E-63	Armak	Cationic, CSS emulsifier, amine	
Jetco AE-7	Jetco Chemicals Company P.O. Box 1278	Cationic, CSS emulsifier quaternary amine	
Tyfo A	Nacco 14439 South Avalon Gardena, CA. 90248 213-515-1700	Cationic, CQS-CSS emulsifier, amine	
Tyfo B	Nacco	Cationic, CQS-CSS emulsifier, lignin derivitive	
Arosurf AA-54	Sherex	Cationic, CRS amine	
Arosurf AA-55	Sherex	Cationic, CRS amine	
Arosurf AA-60	Sherex	Cationic, CRS amine	
Redicote E-67	Armak	Cationic, CRS amine with viscosity builder	
Jetco AE 6	Jetco	Cationic, CRS amine	
Redicote E-4868	Аглак	Cationic, CSS amine	
Redicote AP	Armak	Internal dispersant for asphalt, amine	
Varonic Q 230	Sherex	Emulsifier, ethoxylated coco amine	
Varonic T 225	Sherex	Emulsifier, ethoxylated tallow amine	
Redicote E-64	Amak	Cationic, CRS amine	
Tergitol 15-5-9	Union Carbide Corporation 270 Park Avenue New York, N.Y. 10017 212-695-5054	Emulsifier/dispersant ethoxylated nonyl phenol	
Varion CAS	Sherex	Emilsifier, coco sulfoberaine	
G-752	Sherex	Emulsifier, ethoxylated amine	

11

3.3 Findings During Emulsion Formulation Experiments

During the emulsion formulation and production phase of the project, several important observations and findings regarding SEA and Sulphlex emulsion production characteristics were noted. Details of the findings briefly discussed below are contained in Appendix A.

During emulsion formulation experiments, it was found that it was very difficult to clean emulsion mills after making SEA or Sulphlex emulsion. Stainless steel piping is required in the mill as sulfur corrodes copper. The cleaning procedure which was used consists of flushing the mill with asphalt immediately after making SEA or Sulphlex emulsion to remove sulfur from the mill system.

Very early during emulsion formulation experiments it was determined that there were actually three types of base stocks being studied instead of two; SEA below 20 percent sulfur (all sulfur is soluble in asphalt), SEA above 20 percent sulfur (dissolved sulfur plus free sulfur in the asphalt), and Sulphlex.

The first step in developing SEA and Sulphlex emulsions was to determine whether or not standard asphalt emulsion formulations could be used. They could not. Emulsions which were produced using standard formulations failed. However, it was determined that satisfactory anionic emulsions could be made from SEA base stocks containing 15 percent or less sulfur by using increased emulsifier concentrations. Also, it was noted early during formulation studies that emulsions made with base stocks containing sulfur settled to a greater extent than asphalt emulsions. This may be attributed to the higher specific gravity of SEA and Sulphlex when compared to asphalt cement.

For an emulsifier to be effective, one part of the emulsifier must be soluble in the base stock phase, and another part in the water phase. A major problem in this project was to find emulsifiers that would function properly with sulfur. It was found that addition of PAMAK WCFA (a tall oil based anionic rapid set emulsifier) to sulfur or Sulphlex and reaction at 275F (135C) for two hours prior to emulsification would greatly improve the quality of emulsions produced. Addition and reaction of PAMAK WCFA to a SEA mixture just prior to emulsification did not result in emulsions as high in quality as when the PAMAK WCFA is added and reacted separately with sulfur and asphalt. These findings enabled production of successful SEA emulsions at sulfur contents above 20 percent and the production of a successful Sulphlex emulsion.

A second problem was that of reducing SEA and Sulphlex emulsion settlement. The addition of Natrosol 250 HR, a hydroxyethyl cellulose viscosity builder, reduced settlement in SEA emulsions. The Natrosol 250 HR increases the viscosity of the continuous phase (water portion) which tends to reduce the rate of settlement of the dispersed phase (SEA or Sulphlex) with either anionic or cationic emulsions. Additionally, since rate of settlement and particle movement is reduced, emulsion stability is increased. Natrosol 250 HR is commonly used in the paint industry to reduce settlement.

The addition of Redicote AP, an amine which functions as an internal dispersant, to asphalt prior to emulsification with sulfur which had been reacted with PAMAK WCFA was found to improve quality of cationic emulsions containing SEA base stocks.

During production of catonic SEA emulsions, it was found that heat is detrimental to emulsion quality. Experimentation showed that the length of time an emulsion is stored at elevated temperatures can influence quality. Longer time periods at elevated temperatures resulted in decreased quality as evidenced by early breaking. The effects of heat on quality were more pronounced with the cationic emulsions studied than with the anionics.

3.4 Emulsion Formulations

Details of emulsion formulation and quality of emulsions produced are contained in Appendix A. Fourteen different successful emulsions were produced and characterized in the laboratory.

4.0 PHYSICAL CHARACTERISTICS OF SULFUR-EXTENDED-ASPHALT AND SULPHLEX EMULSIONS

4.1 Data Analyses

Sulfur-extended-asphalt (SEA) and Sulphlex emulsion formulations having adequate stability and resistance to breaking were physically characterized according to ASTM D244. Modifications were made to several of the test procedures to accommodate unique characteristics of the sulfur-water emulsions. A major modification, outlined in Appendix B, was the development of a modified distillation procedure. Several nonstandard test procedures were also used. Tests were performed in duplicate and results analyzed statistically using conventional one-way analysis of variance (ANOVA) techniques.

The model for the analyses is:

 $Y_{ii} = \mu + E_i + \varepsilon_{ii}$

in which:

Yii	=	response variable
¯μ	=	effect of overall mean
Ei	=	effect of emulsion type
ij	-	experimental error

The experimental analysis matrix is shown in Figure 2. For several of the emulsions, it was not possible to perform all tests due to the emulsion breaking before completion of testing or due to testing problems related to emulsion characteristics. Therefore, degrees of freedom for the ANOVA vary depending on the number of emulsions tested for each test procedure. Prior to ANOVA, cell homogeneity was checked using the Foster and Burr Q-test (18). Cell variances for all data were found to be homogeneous, therefore, data transformations were not required.

If emulsion type was found to be a significant effect, the data were ranked using the Newman-Keuls multiple range test (19) to determine where differences existed. Data, means (\bar{x}) , standard deviations (s), coefficients of variation (CV), ANOVA summaries, and Newman-Keuls results for emulsion properties are contained in Appendix C.

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CSS10		
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RS30		1
SS 30		1
RS15		
SS15		1
RS10	1	
SS10		
* RS10		
* SS10	1	1

*Note: PAMAK WCFA not reacted with sulfur.

FIGURE 2 Experimental Analysis Matrix

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4.2 Emulsions Tested

Fourteen different modified sulfur-water emulsions were characterized. These emulsions and their formulations are tabulated in Table 5. The SS 10* and RS 10* emulsions were produced early in the study prior to finding that reaction of PAMAK WCFA with the sulfur at 275F (135C) for a minimum of two hours prior to emulsification would greatly improve emulsion quality. The second set of SS 10 and RS 10 percent SEA emulsions were formulated with PAMAK WCFA reacted with the sulfur.

Storage stability tests were not performed with the cationic emulsions due to insufficient sample size. The cationic emulsions were produced in one quart batches so that they would cool quickly enough to prevent the emulsion from failing as explained in Section 3.3. All other emulsions were produced in five gallon batches. During testing, the RS 10* and RS 30 percent SEA emulsions began to break. Consequently, storage stability, water miscibility, demulsibility, and ductilities with the RS 10* emulsion, and the distillation residue penetration with the RS 30 were not performed.

All of the cationic emulsions boiled over during the distillation procedure possibly due to the high concentrations of cationic emulisifiers used in their formulations. Therefore, residue and water contents by distillation, and physical characteristics of distillation residues could not be determined for the cationic emulsions.

All tests with the Sulphlex residues except for penetration of the distillation residue were not performed due to evolution of strong fumes during heating.

4.3 Water Content

Water content of emulsions was determined using both distillation and evaporation procedures. The standard ASTM D244 distillation procedure (Sections 8 to 10) was not used as it requires heating the emulsion to 500F (260C). Heating to this temperature would result in H_2S and SO_2 evolution and possible excessive hardening of the binders.

Emulsion Designations and Formulations Which Were Characterized

Emulsion Designation	Base Stock	Emulsifiers
SS 10 ^{*1}	10% SEA	2% ² Vinsol NVX, 0.7% Marasperse CE, 0.15 % Natrosol 250 HR
RS 10 ^{*1}	10% SEA	0.75% PAMAK WCFA (in asphalt), 0.3% PAMAK WCFA added to sulfur, 0.25% Natrosol 250 HR
SS 10	10% SEA	0.18% PAMAK WCFA (in sulfur) ³ , 0.54% PAMAK WCFA (in asphalt), 0.06% Natrosol 250 HR, 2.0% Vinsol NVX, 0.6% Marasperse CE
RS 10	10% SEA	0.18% PAMAK WCFA (in sulfur) ³ , 0.70% PAMAK WCFA (in asphalt), 0.06% Natrosol 250 HR
SS 15	15% SEA	2.2% Vinsol NVX, 0.08% Marasperse CE, 0.08% Natrosol 250 HR
RS 15	15% SEA	0.3% PAMAK WCFA (in sulfur) ³ , 0.7% PAMAK WCFA (added to asphalt), 0.07% Natrosol 250 HR
SS 30	30% SEA	2.5% Vinsol NVX, 0.54% PAMAK WCFA (in sulfur) ³ , 0.84% PAMAK WCFA (in asphalt)
RS 30	30% SEA	0.54% PAMAK WCFA (in sulfur) ³ , 1.50% PAMAK WCFA (in asphalt), 0.075% Natrosol 250 HR
RS 40	40% SEA	0.74% PAMAK WCFA (in sulfur) ³ , 3.50% PAMAK WCFA (in asphalt), 0.6% Natrosol 250 HR
CSS 10	10% SEA	0.24% PAMAK WCFA (in sulfur) ³ ,0.54% Redicate AP (in asphalt), 2.0% Sherex AA57, 0.06% Natrosol 250 HR, 0.001% 35% HCL
CRS 10	10% SEA	0.24% PAMAK WCFA (in sulfur) ³ ,0.54% Redicate AP (in asphalt), 2.0% Sherex AA54, 0.06% Natrosol 250 HR, 0.8% 35% HCL
CSS 15	15% SEA	0.35% PAMAK WCFA (in sulfur) ³ ,0.51% Redicate AP (in asphalt), 2.0% Sherex AA57, 0.06% Natrosol 250 HR, 0.001% 35% HCL
CRS 15	15% SEA	0.35% PAMAK WCFA (in sulfur) ³ ,0.51% Redicate AP (in asphalt), 2.0% Sherex AA54, 0.06% Natrosol 250 HR, 0.8% 35% HCL
RS SX	Sulphlex 233 CDC	2% PAMAK WCFA (in Sulphlex) ³ , 1% (based on (Sulphlex) PAMAK WCFA neutralized with NaOH in soap solution, sufficient caustic to neutralize PAMAK WCFA in Sulphlex

² Emulsifier percentages are based on total emulsion weight

³PAMAK WCFA reacted with sulfur two hours (minimum) at 275F prior to emulsification

Therefore, a modified distillation procedure was developed which consisted of heating the emulsions to 260F (127C) and sweeping with CO₂. Details of this distillation procedure are contained in Appendix B. The ASTM D244 evaporation procedure (Sections 14 to 18) was followed for water content determinations by evaporation except that the evaporations were performed at 275F (135C) instead of the stipulated 325F (163C) to prevent excessive H_2S and SO₂ evolution and possible binder hardening.

Water content by distillation results are tabulated in Appendix C in Table 12 and the ANOVA summary in Table 13. Emulsion type was a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 11) shows that water content of the RS Sulphlex emulsion was the highest (47.1% average) and that the RS 40 and RS 30 percent SEA emulsions were similar and had the lowest water contents (31.3% average). Other differences were noted as shown in Figure 11.

Water content by evaporation results are tabulated in Appendix C in Table 14 and the ANOVA summary in Table 15. Emulsion type was a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 12) shows that the water content of the CSS 10 percent SEA emulsion was the highest (42.2%) and that the RS 30 and RS 40 percent SEA emulsions were similar and had the lowest water contents (31.6% average). Other differences were noted as shown in Figure 12.

4.4 Storage Stability

Storage stability tests were performed in accordance with the ASTM D244 procedure (Sections 56 to 62) except that the evaporations for determining residue contents were performed at 275F (135C) instead of the stipulated 325F (163C). Storage stability test results are tabulated in Appendix C in Table 16. The data reported are the difference in residue content of the emulsion from top to bottom of the graduated cylinder, and reflect the degree of residue settlement of the emulsion or the degree of permanence of the dispersion (14). Higher numbers indicate a greater degree of settlement than lower numbers. The ANOVA summary for storage stability is tabulated in Table 17. Emulsion is a significant effect at the 0.01 level. Newman-Keuls ranking (Figure 13) shows that the RS Sulphlex emulsion had the highest amount of settlement (60.0% average storage stability value) and that the RS 40 percent SEA emulsion had the second highest (33.3% average storage stability value). The storage stabilities of the other emulsions tested were not statistically different (0.20% average). These observations can be seen in Figure 3. Higher amounts of settlement are noted for sulfur concentrations above 30 percent.

4.5 Freeze-Thaw

Freeze-thaw tests were performed in accordance with the ASTM D244 procedure (Section 49) except that the emulsions were examined after each of the three freeze-thaw cycles. The test indicates the resistance of an emulsion to breaking due to being frozen. Test results are tabulated in Appendix C in Table 18. Statistical analyses was not performed with the data. Data in Table 18 indicate that only the two SS 10 percent and the RS 30 percent SEA emulsions did not break as a result of the three freeze-thaw cycles. The RS 15 percent SEA emulsion did not break after the first freeze-thaw cycle, but did after the second. All other emulsions tested broke during the first freeze-thaw cycle.

4.6 Emulsion Break Time

Emulsion break time when mixed with aggregate was determined by hand mixing the emulsion with aggregate for five minutes, placing the mixture on a sheet of release paper, and subjectively determining the break time by visual examination. Break of the emulsion was evaluated based on the color change from brown to black. Aggregate used in the tests was a crushed granite from the Graniterock quarry at Aromus, California. Aggregate gradation used in tests and aggregate specific gravity and absorption are tabulated in Table 6. A four percent residue content (based on an equivalent asphalt cement volume as calculated by specific gravities) was used in all determinations. Emulsion residue specific gravities were calculated based on emulsion specific gravities measured using a 250 ml volumetric flask and the residue content by evaporation. Emulsion and residue specific gravities are tabulated in Table 7.



FIGURE 3 Storage Stability versus Percent Sulfur in Binder

GRADATION, SPECIFIC GRAVITY, AND ABSORPTION OF GRANITEROCK AGGREGATE USED IN EMULSION BREAK TIME DETERMINATIONS

<u>Sieve Size</u>

% Passing

in	(19.0	mm)	100
in	(12.5	mm)	75
in	(9.5	mm)	50
in	(6.3	mm)	25
4	(4.75	mm)	0
	in in in 4	<pre>in (19.0 in (12.5 in (9.5 in (6.3 4 (4.75</pre>	<pre>in (19.0 mm) in (12.5 mm) in (9.5 mm) in (6.3 mm) 4 (4.75 mm)</pre>

Bülk	Specific	Gravity	2.835
Absor	ption		1.1%

SPECIFIC GRAVITIES OF EMULSIONS AND RESIDUES

Emuls	<u>sion</u>	Measured ¹ Emulsion S.G.	Calculated ² Residue S.G.
SS	10*	1.054	1.094
RS	10*	1.053	1.084
SS	10	1.052	1.091
RS	10	1.053	1.084
SS	15	1.073	1.123
RS	15	1.068	1.107
SS	30	1.116	1.201
RS	30	1.134	1.202
RS	40	1.118	1.186
CSS	10	1.042	1.076
CRS	10	1.042	1.070
CSS	15	1.049	1.088
CRS	15	1.049	1.081
RS	SX	1.124	1.263

Note:

*PAMAK WCFA not reacted with sulfur.

 $1_{\mbox{Measured}}$ volumetrically using a 250 ml pycometer at 77F

 2 Calculations based on evaporation residue content

22

Emulsion break time test results are tabulated in Appendix C in Table 19 and the ANOVA summary in Table 20. Emulsion is a significant effect at the 0.01 level. Newman-Keuls ranking (Figure 14) shows that the CSS 10 percent SEA emulsion had the longest break time (39.3 minutes) and that the RS 10* percent SEA emulsion had the shortest (0.5 minutes). The ranking also shows that break times of the cationic emulsions, even the cationic rapid sets, were longer than those of the anionics. The cationics foamed during mixing, which may have caused the longer break times. The anionic rapid set emulsions, except for the RS Sulphlex emulsion, had the shortest break times (less than 6 minutes).

4.7 Viscosity

Viscosity tests were performed in accordance with the ASTM D244 procedure (Sections 22 to 24) using the Saybolt Furol viscometer. Test results at 77F (25C) are tabulated in Appendix C in Table 21 and the ANOVA summary in Table 22. Emulsion is a significant effect at the 0.01 level. Newman-Keuls ranking (Figure 15) shows that the SS 10* percent SEA emulsion had the highest viscosity (226 seconds) and that the CRS 10, CSS 15, CSS 10, CRS 15, and RS 40 percent SEA emulsions and the RS Sulphlex emulsion were not different and had the lowest viscosity (25.3 seconds average). Other differences were noted as shown in Figure 15. Additionally, for comparison to ASTM D2397, "Standard Specification for Cationic Emulsified Asphalt," tests at 122F (50C) were per- formed with the CRS 10 and CRS 15 percent SEA emul- sions. Average viscosity for the CRS 10 percent SEA emulsion was 15.5 seconds and for the CRS 15, 25.3 seconds.

4.8 <u>Coating Ability</u>

Coating ability tests were performed in accordance with the ASTM D244 procedure (Sections 50 to 55). This test is designed for medium setting emulsions to determine the ability of the emulsion to coat the aggregate thoroughly, withstand mixing action, and withstand washing after completion of mixing (17). It is not applicable to rapid or slow setting emulsions (14), however, it was performed with the emulsions in this study to determine the compatibility of the formulated emulsions with aggregate. Aggregate used in the tests was the crushed granite from the Graniterock quarry at Aromus, California and was of the same gradation used in break time determinations (Table 7).

Test results for both dry and wet aggregates are tabulated in Appendix C in Table 23. All emulsions yielded a "good" initial coating (per ASTM D244) with dry aggregate. All of the slow set emulsions washed off of the aggregate yielding a poor rating after rinsing. This is expected since the slow sets would not have had time to break prior to rinsing. The RS 15 percent SEA emulsion with dry aggregate yielded a good rating after rinsing indicating that it had broken on the aggregate surface. The other rapid sets yielded either poor or fair ratings indicating that they did not break on the aggregate surface during the test.

For tests with wet aggregate all emulsions except the RS 10 and RS 15 percent SEA's yielded initial coatings rated as good. The RS 10 and RS 15 were rated as poor. All slow set emulsions received poor ratings after rinsing, again, as would be expected. The CRS 10 and CRS 15 percent SEA emulsions yielded coatings after rinsing rated as good. Other rapid set emulsions yielded coatings after rinsing rated as either fair or poor.

4.9 Modified Water Miscibility

Modified water miscibility tests were performed in accordance with the ASTM D244 procedure (Sections 45 to 48). The test is designed to determine if medium or slow setting emulsions can be mixed with water (17). It is not applicable to rapid setting emulsions (14). The test was performed with all emulsions formulated since setting characteristics were not precisely known.

Test results are tabulated in Appendix C in Table 24 and the ANOVA summary in Table 25. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 16) shows that the water miscibilities of the CSS 15, CSS 10, CRS 15, RS 10, and SS 15 percent SEA emulsion were not different and that these emulsions experienced the greatest degree of separation (47.5% average). The RS 30 and RS 15 percent SEA emulsions and the RS Sulphlex emulsion were not different and had the least separation (10.4% average). Other differences shown in Figure 16 are noted. These observations are plotted in Figure 4.

4.10 Residue Content

Residue contents of the emulsions were determined using three procedures - distillation, evaporation, and demulsification. The distillation and evaporation procedures used are as discussed in Section 4.2. The ASTM D244 demulsification procedure (Sections 25 to 28) using as appropriate calcium chloride or dioctyl sodium sulfosuccinate solutions was employed for demulsibility determinations.

Residue content by distillation test results are tabulated in Appendix C in Table 26 and the ANOVA summary in Table 27. During the distillation procedure, all cationic emulsions foamed excessively and boiled over. Therefore, residue contents by distillation could not be determined for the cationic emulsions. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 17) shows that the RS 30 and RS 40 percent SEA emulsions were similar and had the highest residue content (68.8% average). The RS Sulphlex emulsion had the lowest residue content (52.9%). Several other differences are noted in Figure 17.

Residue content by evaporation test results are tabulated in Appendix C in Table 28 and the ANOVA summary in Table 29. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 18) shows that the RS 30 and RS 40 percent SEA emulsions were similar and had the highest residue content (68.4% average). The SS 10, CSS 15, and CSS 10 percent SEA emulsions were similar and had the lowest residue content (58.0% average). Other differences were noted as shown in Figure 18.

A comparison of residue contents by distillation and evaporation is shown in Figure 5. From Figure 5, it can be seen that slight differences in residue contents determined by the two procedures exist, especially with the Sulphlex emulsion. The higher residue content by evaporation with the Sulphlex emulsion may be due to the evaporation procedure not removing all of the water in the emulsion.







FIGURE 5 Comparison of Residue Contents by Distillation and Evaporation
The demulsibility test indicates the relative rate at which the colloidal asphalt globules break when spread in thin films and is applicable to rapid and medium setting emulsions (14). The 1.11g/liter CaCl₂ solution was used with anionic rapid set emulsions and the 8.00g/liter dioctyl sodium sulfosuccinate solution with both cationic rapid set and cationic slow set emulsions. The 5.55g/liter CaCl₂ solution was used with anionic slow set emulsions. Once again, it is noted that since the setting characteristics of the emulsions were not precisely known, testing was performed with all emulsions formulated. Test results indicate the percent of the residue content determined by the distillation procedure that was broken by the demulsification solutions (14). Since residue contents by distillation could not be determined for the cationic emulsions, residue contents by evaporation were used in calculations for the cationics. A high degree of demulsibility is desired for rapid set emulsions (14).

Demulsibility test results are tabulated in Appendix C in Table 30 and the ANOVA summary in Table 31. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 19) shows that the anionic rapid set emulsions had greater degrees of demulsibility than the slow set emulsions, as expected. The RS 10 and RS 15 percent SEA emulsions were similar and had the highest degree of demulsibility (72.5% average). The SS 30, SS 10, and all cationic SEA emulsions were similar and had the lowest degree of demulsibility (0.4% average). Other differences as shown in Figure 19 are noted. Figure 6 is a plot of demulsibility versus sulfur content of the binder for anionic rapid set emulsions tested. From Figure 6, it can be seen that as percent sulfur increases, demulsibility tends to decrease.

4.11 Long Term Stability

The long term stability of the emulsions was evaluated by visually examining their consistency and determining if settlement could be stirred back into the emulsion to give a homogeneous, unbroken product. Observations are tabulated in Appendix C in Table 32.





Emulsion age at examination varies from 1.5 to 12 months, so comparisons of emulsions of different ages cannot be made. Commercial emulsions are generally used within 30 days of production. However, examination of emulsions after a long period can give an indication of the relative resistance of the emulsions to breaking. Of the emulsions which were 12 months old, the SS 15 and RS 15 percent SEA emulsions settled. However, the settlement could be restirred into the emulsion producing a homogeneous mixture indicating that they had not broken. The other 12 month old emulsions contained hard settlement and had either slightly or totally broken. The 3 month old RS 10 and SS 10 percent SEA emulsions were not broken and contained only a slight amount of settlement when examined. The RS Sulphlex emulsion showed signs of breaking and separation when examined at an age of 7 months. The 1-1/2 month old cationic emulsions had not broken and experienced only a slight amount settlement, except for the CSS 15 percent SEA emulsion which was beginning to show signs of breaking (presence of small coagulated particles).

5.0 PHYSICAL CHARACTERISTICS OF SULFUR-EXTENDED-ASPHALT AND SULPHLEX EMULSION RESIDUES

5.1 Data Analyses

Emulsion residues obtained from the distillation and evaporation procedures were characterized using penetration (ASTM D5) at 77F (25C), absolute viscosity (ASTM D2171) at 140F (60C), and ductility (ASTM D113) at 77F (25C). Tests were performed in duplicate and results analyzed statistically using conventional one-way ANOVA techniques. The model and analysis procedure used are the same as discussed in Section 4.1. Data, means (\bar{x}), standard deviations (s), coefficients of variation (CV), ANOVA summaries, and Newman-Keuls ranking results for residue characteristics are contained in Appendix D.

5.2 Residue From Distillation

Penetrations at 77F (25C) of distillation residues are tabulated in Appendix D in Table 33 and the ANOVA summary in Table 34. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 20) shows that the SS 10*, RS 10, RS 15, RS 30 and RS 10* percent SEA emulsions were similar and had the highest penetration (105 average). The RS Sulphlex emulsion had a penetration of 8 which was the lowest of all residues tested. Other differences are noted in Figure 20. Penetrations of RS and SS emulsion residues tested are plotted in Figure 7. From Figure 7, it can be seen that as sulfur concentration in the binder increases, penetration decreases for rapid set emulsions, but tends to increase for slow sets.

Absolute viscosities of distillation residues at 140F (60C) are tabulated in Appendix D in Table 35 and the ANOVA summary in Table 36. Viscosities for residues with 30 and 40 percent sulfur could not be obtained due to sulfur separation in the viscometer. Emulsion is a significant effect at the 0.01 level. Newman-Keuls ranking (Figure 21) shows that the SS 10 percent SEA emulsion had the highest viscosity (1656 poise) and that the SS 15, RS 15, SS 10*, and RS 10 percent SEA emulsion were similar and had the lowest viscosity (856 poise average). Additionally, the RS 10*, SS 15, and RS 15 percent SEA emulsions were similar (952 poise average).





Penetration at 77F (25C) of SS and RS Emulsions

Ductilities at 77F (25C) of distillation residues are tabulated in Appendix D in Table 37 and the ANOVA summary in Table 38. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 22) shows that the SS 10* and RS 10 percent SEA emulsions had the highest ductility (both were 100 + cm) and that the SS 30, SS 15, and RS 40 percent SEA emulsions were similar and had the lowest ductility (31 cm average). Other differences shown in Figure 22 are noted. Ductilities of anionic RS and SS emulsions are plotted in Figure 8. From Figure 8, it is noted that as percent sulfur in the binder increases, ductility tends to decrease.

5.3 Residue From Evaporation

Penetrations at 77F (25C) of evaporation residues are tabulated in Appendix D in Table 39 and the ANOVA summary in Table 40. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 23) shows that the CSS 10, CRS 15, CSS 15, RS 10* and RS 10 percent SEA emulsions were similar and had the highest penetrations (125 average). The SS 15, RS 30, SS 30, and RS 40 percent SEA emulsions were similar and had the lowest penetrations (66 average). Other differences are noted in Figure 23. Penetration results are plotted in Figure 9. From Figure 9, it is noted that for both anionic and cationic slow set and anionic rapid set emulsions, as percent sulfur in the binder increases, penetrations tend to decrease.

Absolute visosities at 140F (60C) of evaporation residues are tabulated in Appendix D in Table 41 and the ANOVA summary in Table 42. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 24) shows that the SS 10, CRS 10, CSS 10, CSS 15, SS 15, and SS 10* percent SEA emulsions were similar and had the highest viscosities (1429 poise average). The RS 10, RS 10*, and RS 15 percent SEA emulsions were similar and had the lowest viscosities (712 poise average). Other differences are noted in Figure 24.

Ductilities at 77F (25C) of evaporation residues are tabulated in Appendix D in Table 43 and the ANOVA summary in Table 44. Emulsion is a significant effect at the 0.01 confidence level. Newman-Keuls ranking (Figure 25) shows that the SS 10, RS 10, RS 40, and all cationic emulsions were not different









and had the highest ductilities (all 100 + cm). The SS 30 and RS 15 percent SEA emulsions were similar and had the lowest ductilities (19 cm average). Other differences are noted in Figure 25.

- 6.0 COMPARISON OF PROPERTIES OF SULFUR-EXTENDED-ASPHALT AND SULPHLEX EMULSIONS TO ASTM D977 AND D2397 REQUIREMENTS
 - 6.1 In order to more adequately conceptualize the characteristics of the SEA and Sulphlex emulsions formulated and produced during this study, properties of the modified sulfur-water emulsions were compared to ASTM D977, "Standard Specification for Emulsified Asphalt" and D2397, "Standard Specification for Cationic Emulsified Asphalt" (17) requirements.

Properties of anionic slow set SEA emulsions and ASTM D977 specification requirements for SS-1 and SS-lh emulsions are tabulated in Table 8. From Table 8, it can be seen that the SS 10 percent SEA emulsion meets viscosity, storage stability, residue content, and penetration and ductility of residue requirements for an SS-lh emulsion. The SS 10* percent SEA emulsion (formulated without the sulfur reacted with PAMAK WCFA) meets the above requirements except for viscosity (226 seconds compared to the specification requirement of 20 to 100 seconds). The SS 15 percent SEA emulsions meets requirements for a SS-lh except for residue ductility. The SS 30 emulsion meets requirements for an SS-1 except for residue ductility. The cement mixing test, sieve test, and solubility of residue were not determined and therefore could not be compared.

Properties of anionic rapid set SEA and Sulphlex emulsions and ASTM D977 specification requirements for RS-1 emulsions are tabulated in Table 9. The sieve test and residue solubility were not performed and therefore could not be compared. The RS 10 and RS 15 percent SEA emulsions met requirements for an RS-1 emulsion. The RS 40 percent SEA and RS Sulphlex emulsions did not meet storage stability, demulsibility or residue penetration requirements. Several other areas of nonconformance were noted with other emulsions as indicated in Table 9.

Properties of cationic slow set SEA emulsions and ASTM D2397 specification requirements for CSS-1 emulsions are tabulated in Table 10. Since the distillation test could not be performed with the cationic emulsions, residue content and residue penetration and ductility values used for comparison were those obtained by the evaporation procedure.

COMPARISON OF ANIONIC SLOW SET SEA EMULSION PROPERTIES TO SEVERAL ASTM D977 REQUIREMENTS FOR SS-1 EMULSIONS

Property	<u>SS 10*</u>	<u>SS 10</u>	<u>SS 15</u>	<u>SS 30</u>	Specification Limits
Tests on Emulsion:					
Viscosity, Saybolt Furol, 77F (25C); s	226	72.2	45.4	66.6	20-100
Storage Stability 24 hr; %	0.6	0.5	0.25	0.20	l max
Residue by Distillation; %	59.7	59.5	62.1	62.2	57 min
<u>Tests on Residue</u> :					
Penetration, 77F (25C), 100g, 5 sec; 1/10 mm	114	75	73	101	100-200 or 40-90 ¹
Ductility, 77F (25C), 5 cm/min; cm	n 100+	68	33	34	40 min

Note: 1Requirement for SS-lh emulsion.

COMPARISON OF ANIONIC RAPID SET SEA AND SULPHLEX EMULSION PROPERTIES TO SEVERAL ASTM D977 REQUIREMENTS FOR RS-1 EMULSION

		Emuls	sion De	signat	ion		Spec.
Property	<u>RS 10</u> *	<u>RS 10</u>	<u>RS 15</u>	RS 30	<u>RS 40</u>	RSSX	Limits
Tests on Emulsion:							
Viscosity, Saybolt Furol, 77F (25C); s	44.6	44.5	70.7	131	20.2	19.1	20-100
Storage Stability 24 hr; %	2 -	0.3	0.15	-0.7	33.3	60.0	l max
Demulsibility, 35ml, 0.02N, CaCl ₂ ; %	71.6	75.9	69.1	34.6	28.6	31.2	60 min
Residue by Distillation; %	65.0	64.8	66.0	70.3	67.2	52.9	55 min
Tests on Residue:							
Penetration, 77F (25C), 100g, 5 sec; 1/10 mm	86	113	113	-	65	8	100-200
Ductility, 77F (25C), 5 cm/min;	cm -	100+	41	37	25	_	40 min

COMPARISON OF CATIONIC SLOW SET SEA EMULSION PROPERTIES TO ASTM D2397 REQUIREMENTS FOR CSS-1 EMULSIONS

Property	<u>CSS 10</u>	CSS 15	Specification Limits
Tests on Emulsifier:			
Viscosity, Saybolt Furol at 77F (25C); s	26.0	28.1 ¹	20-100
Residue Content; %	57.4 ¹	57.8 ¹	57 min^2
Tests on Residue:			
Penetration, 77F (25C) 100g, 5s; 1/10 mm	148 ³	118 ³	100-250 ⁴
Ductility, 77F (25C), 5 cm/min; cm	100+ ³	100+ ³	40 min ⁴

Notes:

¹Determined by the evaporation procedure ²Specified by the distillation procedure ³Determined on evaporation residue ⁴Specified by distillation residue While differences in results by evaporation and distillation may occur, the evaporation data were used so that comparisons could be made. Storage stability, particle charge, sieve test, cement mixing test, and residue solubility were not determined. Both the CSS 10 and CSS 15 percent SEA emulsions meet viscosity, residue content, and residue penetration and ductility requirements for a CSS-1 emulsion.

Properties of cationic rapid set SEA emulsions and ASTM D2397 specification requirements for CRS-1 emulsions are tabulated in Table 11. Evaporation residues were used for comparison purposes as results for the distillation procedure could not be obtained. Storage stability, particle charge, classification test, sieve test, and residue solubility were not determined. The CRS 15 percent SEA emulsion meets viscosity, residue content and residue penetration and ductility requirements for a CRS-1 emulsion. The CRS 10 percent SEA emulsion does not meet viscosity (15.5 seconds compared to the 20 to 100 second specification requirement) or residue penetration (98 compared to the 100 to 250 specification requirement) requirements.

COMPARISON OF CATIONIC RAPID SET SEA EMULSION PROPERTIES TO ASTM D2397 REQUIREMENTS FOR CRS-1 EMULSIONS

Property	<u>CRS 10</u>	<u>CRS 15</u>	Specification
<u>Tests on Emulsifier</u> :			
Viscosity, Saybolt Furol, 122F (50C); s	15.5	25.3	20-100
Residue Content; %	61.6 ¹	62.0 ¹	60 min^2
Tests on Residue:			
Penetration, 77F (25C) 100g, 5s; 1/10 mm	′ 98 ³	129 ³	100-2504
Ductility, 77F (25C), 5 cm/min; cm	100+ ³	100+ ³	40 min 4

Notes:

¹Determined by the evaporation procedure ²Specified by the distillation procedure ³Determined on evaporation residue ⁴Specified by distillation residue

7.0 CONCLUSIONS

- 7.1 Based on the emulsion formulation experiments and physical testing performed during this investigation, it is concluded that stable modified sulfur-water emulsions can be produced which have physical properties comparable to standard asphalt emulsions currently used in highway construction. Sulphurextended-asphalt binders with up to 40 weight percent sulfur content and Sulphlex can be used as base stocks. Anionic SEA emulsions studied during this investigation were the most successful in terms of ease of production, emulsion stability, and similarity to standard asphalt emulsions. The study has shown that many interactions between emulsion components and production techniques exist which will need to be considered during production of modified sulfur-water emulsions. Several specific conclusions regarding emulsion formulations with SEA and Sulphlex binders and characteristics of resulting emulsions were reached.
 - During production of either SEA or Sulphlex emulsions, reacting the molten sulfur component with a tall oil (PAMAK WCFA) prior to emulsification greatly improves emulsion quality.
 - Addition of a viscosity builder (Natrosol 250 HR) to modified sulfur-water emulsions reduces settlement.
 - Successful cationic SEA emulsions are more difficult to formulate than successful anionic SEA emulsions.
 - As the percentage of sulfur in the emulsion increases, the difficulty in formulating successful emulsions increases.
 - 5. Emulsion residue contents determined by the modified distillation and evaporation test procedures were slightly different.
 - As the percent sulfur in rapid set anionic SEA emulsions increases, emulsion demulsibility decreases.
 - 7. As the percent sulfur in anionic SEA emulsion residues increases, penetrations and ductilities tend to decrease indicating harder materials.
 - 8. As the percent sulfur in the SEA emulsions increases, greater settling of the emulsion is observed.

8.0 RECOMMENDATIONS FOR FUTURE RESEARCH

- 8.1 This study has demonstrated that stable emulsions using either sulfur-extended-asphalt or Sulphlex as base stocks can be produced. During the study, many observations were made regarding emulsion production and testing which deserve further attention.
 - Develop methods to increase or improve the dispersion of sulfur in asphalt prior to or during emulsification which could possibly reduce emulsion settlement and improve ease of formulation.
 - 2. Further investigate the beneficial reaction of the tall oil with sulfur when producing SEA or Sulphlex emulsions.
 - 3. Investigate whether the addition and reaction of tall oil with sulfur in the emulsion modifies properties of resulting emulsion residues.
 - 4. Investigate interactions between emulsifiers which can cause modified setting rates of SEA and Sulphlex emulsions.
 - 5. Develop more stable cationic SEA emulsions and further investigate the detrimental effects of heat on the cationic emulsions produced during this investigation.
 - Investigate the properties of SEA and Sulphlex emulsion-aggregate mixtures for various paving uses such as surface, base, and open graded friction courses.
 - Develop a test procedure for measuring the viscosity of SEA emulsions containing greater than 20 percent sulfur in the base stock.

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APPENDIX A EMULSION FORMULATION RESEARCH BY ROBERT L. DUNNING

Contents:

Final Report -	Emulsions Prepared From Sulfur- Asphalt Binders Containing 10-40 Percent Sulfur and Sulphlex
Supplement 1 -	Formulation of RS Sulphlex Emulsion

Supplement 2 - Additional Formulation Experiments With Cationic SEA Emulsions

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Highway Binder Materials

from

Modified Sulfur-Water Emulsions.

I. Emulsions Prepared From Sulfur-Asphalt Binders Containing 10-40% Sulfur and Sulphlex

Robert L. Dunning

Project: 1151

Client: Engineers Testing Laboratories

January 1981

Abstract

The purpose of this project was to develop emulsions similar to asphalt emulsion but using sulfur extended asphalt (SEA) and Sulphlex as base stocks. It was found that actually three distinct types of base stocks were being studied, SEA base stocks containing 10 and 15% sulfur, in which the sulfur was disolved in the asphalt, SEA base stocks containing 30 and 40% sulfur, in which some of the sulfur was disolved in the asphalt while the rest was dispersed, and Sulphlex. The emulsifier systems used for asphalt could not be used without modification for the SEA or Sulphlex base stocks. The emulsions settled badly and were quite unstable. Settling was greatly reduced by adding Natrosol 250HR to the water phase, and emulsion quality was greatly enhanced by reacting a tall oil with sulfur or Sulphlex prior to emulsification. Successful anionic emulsions were made from all base stocks, however considerable trouble was encountered in making some of the cationic emulsions. Factorial designed experiments greatly aided the investigations.

TABLE OF CONTENTS

1

2

3

5

5

5

5

6

9

10

15 16

Introduction

Conclusions

General Specific

Experimental

Laboratory Cleaning of Mill Base Stocks Asphalts

Sulphlex

Results and Discussion

Distillation of SEA Emulsions Properties of SEA Base Stocks Development of Disposable Viscometer for Sulphlex Emulsion Formulation Studies

Evaluation of Standard Asphalt Formulations Formulation Considerations Use of Multifunctional Emulsifiers Use of Unsaturated Fatty Acids Effect of a Protective Colloid Effect of Redicote AP Effect of Reaction Conditions of the Sulfur, PAMAK WCFA and Asphalt on Emulsion Quality.

Effect of Time Effect of Temperature Effect of the Presence of Asphalt During Cure Effect of In Situ Neutralization of Emulsifiers

Factorial Designed Experiments

Theoretical CSS Emulsions with 30 and 40% Sulfur SEAs SS Emulsions with 30 and 40% Sulfur SEAs

Mixes With Aggregate

Details of Emulsion Formulations

Emulsions from 10% SEA Base Stock. Slow Set Emulsions from 10% SEA Base Stock. Rapid Set Emulsions from 10% SEA Base Stock. Cationic Slow Set Emulsions from 10% SEA Base Stock. Cationic Quick Set Emulsions from 10% SEA Base Stock. Cationic Rapid Set Emulsions from 15% SEA Base Stock. Slow Set Emulsions from 15% SEA Base Stock. Rapid Set Emulsions from 15% SEA Base Stock. Cationic Slow Set Emulsions from 15% SEA Base Stock. Cationic Slow Set Emulsions from 30 & 40% SEA Base Stock. Slow Set Emulsions from 30 & 40% SEA Base Stock. Rapid Set Emulsions from 30 & 40% SEA Base Stock. Cationic Slow Set Emulsions from 30 & 40% SEA Base Stock. Cationic Rapid Set Emulsions from Sulphlex

Proposed Direction of Future Work

Improving the dispersion of sulfur in the asphalt Adding sulfur as a separate dispersion in the SEA emulsions Investigate the chemistry of the reaction of sulfur with tall oil and amines with and without the presence of asphalt Factorial designed experiments for emulsion formulation studies

Clay Emulsions

INTRODUCTION

The purpose of this project is to develop water emulsions using sulfur extended asphalt (SEA) and plasticized sulfur (Sulphlex) base stocks which might find application in highway construction. These emulsions were to be designed to be comparable to the various grades of asphalt emulsions, namely, rapid, medium and slow setting types, both anionic and cationic.

The base stocks studies were selected to be similar to those reported in the literature 1, with sulfur concentrations of 10-40°, based upon the mixture of asphalt and sulfur=100°, and selected grades of Sulphlex 2) as supplied by Engineers Testing Laboratories and Southwest Research Institute.

In developing the formulations we attempted to produce emulsions which could be readily made commercially with little or no change. We therefore avoided emulsifying equipment which had a very much greater input of energy per unit mass than a commercial mill, and avoided emulsification techniques which would produce a product at a temperature lower than that which one would expect from a commercial mill. This latter point is very important as certain emulsifiers, such as the polyethoxylates, have an inverted solubility, thus emulsions might be readily made at a low temperature, but not be made at a normal emulsifying temperature.

The first area of study were those formulations which are in general use in asphalt emulsions, and expanding and revising those formulas to fit the SEA and Sulphlex base stocks. In our terminology, we used the classification (ie SS for slow set) which was usually associated with a particular emulsifier (ie Vinsol for SS, ARMAK E-67 for CRS, etc.) even if the final emulsion may not have exactly fit the classification. Our challenge was to find ways to emulsify the base stocks with those various catagories of emulsifiers with some very difficult base stocks. For that reason, "SS" type emulsions might in reality behave more like an MS. Future formulation studies will be needed to elucidate all the effects of formulation variables.

As we felt that any product which we should develop should have commercial applications, we did keep cost in mind. In many cases, we found it necessary to use high levels of emulsifiers which will probably reduce the attractiveness of those formulations because of cost. Future work, especially with additives, may show the means to reduce cost, however.

CONCLUSIONS

General

- As the percent of added sulfur increases, the difficulty in making emulsions also increases.
- Adding Natrosol 250HR to the emulsifier solution markedly increases the quality of the emulsion with anionic and cationic emulsions.
- 3. Adding the tall oil PAMAK WCFA to the sulfur extended asphalt or the Sulphlex, and curing the mixture for 2 hours at 275°F or above markedly improved the quality of most anionic and cationic emulsions.
- 4. Adding Redicote AP (an amine made by Armak) was beneficial for certain emulsions.
- 5. While the Sulphlex 233 was the type of Sulphlex available for these studies, it is our opinion that one of the Sulphlexes made with tall oil pitch would be more amenable to emulsification.
- 6. A disposable viscometer may be used to measure the viscosity of the Sulphlex.

Specific

- RS type emulsions can be made from sulfur extended asphalt, to 40% sulfur in the base stock, and from the Sulphlex 233. The emulsifier is PAMAK WCFA, a tall oil, which is added to the base stock and cured for 2 hours before making the emulsion. The formulations include Natrosol 250HR, a hydroxyethylcellulose.
- 2. SS type emulsions can be made from sulfur extended asphalt to 40% sulfur in the base stock and from Sulphlex 233. The emulsifier is Vinsol NVX. PAMAK WCFA was added to the SEA binder and cured as described in (1) above. Natrosol 250HR was used to reduce settlement, and Redicote AP, added to the SEA base stock just prior to making the emulsion, appeared to be beneficial.
- 3. CSS and CRS emulsions were made of the SEA base stocks containing 10 and 15% sulfur, but not at higher levels of sulfur or with the Sulphlex base stock. The formula which worked was based upon Indulin W-3 for the CSS and Armak E-67 for the CRS. Tall oil and the amine Redicote AP were also added to aid emulsification.
- Clay based emulsions made with Sulphlex appeared quite promising.

EXPERIMENTAL

Laboratory Mills

Two laboratory mills were used. In our initial work we used the system shown in Figure 1. The mill consisted of a modified centrifugal pump, two Viking pumps, a soap pot and two asphalt tanks. The emulsion was made by recirculating the soap and adding the sulfur extended asphalt incrementally. The piping was copper tubing which caused considerable problems on the asphalt lines as sulfur reacts with copper, destroying the tubing.

We then set up the system shown in Figure 2, which uses a Charlotte mill. In this case, the speed of the Viking pumps were adjusted so that emulsions of the desired solids content could be produced. Both of the asphalt tanks were used. Sulfur extended asphalt (SEA) and Sulphlex cause considerable contamination problems, thus the SEA or Sulphlex were placed into the smaller auxillary pot and asphalt or an aromatic oil was placed in the larger pot to be used as a purge. This was especially important when running Sulphlex emulsions.

Cleaning of Mills

One of the problems encountered in this project was that of cleaning up the mill, pumps and piping when one wishes to switch back to making straight asphalt emulsions. It was quite inconceivable to use a solvent as dangerous as carbon disulfide, or the halogenated, extremely expensive solvents which will dissolve sulfur. Sulfur is soluble, to a certain extent, in asphalt and aromatic oils however. Two separate methods have been used to clean out the system. In one method, when quart samples of SEA emulsions or Sulphlex emulsions are made, asphalt is used as the solvent. As may been seen in Figure 2, the mill is fed by two asphalt pots. First 2-3 gallons of asphalt are placed into the 18 quart asphalt pot, and recirculated throughout the system. The SEA or Sulphlex base stock is then heated to $275^{\circ}F$ and poured into the smaller pot. Sufficient emulsifier solution is made to make considerably more than the desired quart of emulsion. The soap pump is started, the mill started, then the asphalt is switched into the soap stream and asphalt emulsion is made. The three way valve connecting the small and large pot is then turned to feed the SEA or Sulphlex base stock to the mill. As soon as SEA or Sulphlex emulsion is coming out of the mill, a quart sample is taken, then the valve is turned back to feed the pump with asphalt, again making asphalt emulsion. The mill feed valve for the asphalt is then switched to recirculating, allowing the lines to be full with asphalt. The soap pump continues to flush the mill, after which hot water is used to flush the soap lines and mill.

The second procedure is quite similar to the above, except that instead of using asphalt, a heavy aromatic oil is used, and left in the lines after flushing. When it is necessary to switch back to manufacturing regular asphalt emulsions, we flush the whole asphalt system with hot aromatic oil, including the mill. We have found that oil to be very effective in cleaning out the system.

Base Stocks

<u>Asphalt.</u> Two asphalt base stocks were used; one from U.S. Oil Refining Company in Tacoma, Washington and one from Husky Oil (from their Spokane bulk plant.) The sulfur extended asphalt base stocks were prepared by blending either powdered sulfur or molten sulfur with the asphalt. We found that the preferable method was to add the molten sulfur to the asphalt just prior to preparing the emulsions except when additives were blended into the asphalt sulfur mixture and a cure time was needed.

Sulphlex. The Sulphlex which was primarily used in this study was Sulphlex 233 (CDC soft) which consisted of 70% sulfur, 12% cyclodiene dimer concentrate, 10% dipentene and 8% vinyl toluene. As our studies progressed, it became apparent that we would have been better off if we had been using one of the Sulphlex base stocks which contained tall oil pitch, such as 433, 443 or 453. Modifying the Sulphlex 233 by adding PAMAK WCFA (a tall oil) greatly reduced the problems encountered in making emulsions.

Those of the 400 series had been made only in laboratory quantities, thus they were not available.

Emulsifiers

A wide variety of emulsifiers were used, ranging from anionic, nonionic, cationic and some with more than one active moiety. In the emulsification system we also used viscosity building ingredients. A list of the ingredients in the emulsifier system is shown in Appendix A.

Factorial Designed Experiments

In the later states of this study, factorial designed experiments were set up to unravel the effects of the variables and their interactions. The basic texts which we used were "Design and Analysis of Experiments" by Oscar Kempthorne³) and "Optimization and Industrial Experimentation" by Biles and Swain.⁴) The experiments were 2^n factorial and from k to k replicate. To aid in assessing error we ran four replicates at the center point on one of the experiments. As we were looking for trends, error could also be estimated by assuming that some of the interactions, especially the higher order ones, were very small compared to the primary variables. This probably overestimates the error, thus any effect that appears to be statistically significant probably is.

Each of the variables were transformed so that they could be mapped onto the interval [-1, +1], thus the experiment is confined to intergers in the set $P = \{(a, b, \dots, n) \mid a \in [-1, +1], b \in [1, +1], \dots, n \in [-1, +1], b \in [1, +1], \dots, n \in [-1, +1], with the center point = (0, 0, \dots, 0). The precise design of each experiment will be discussed under the appropriate section under Results and Discussion.$

RESULTS AND DISCUSSION

Distillation of SEA Emulsions

The distillation of the SEA emllsions present a distinct challenge as it is very important that the temperature of the SEA base does not exceed about 300°F. The distillation method described in ASTM D-244 will not work as written since the base oil must be heated to 500°F. To overcome this problem, the D-244 distillation procedure was revised such that the sample was heated to 240-260°F(116-127°C) and swept with CO₂ at 1000ml/min for 15 minutes. As may be seen in Table I, there was essentially no change in the penetrations.

Properties of the SEA Base Stocks

The addition of sulfur to asphalt caused a considerable decrease in the viscosity of the asphalt. Typical data are shown in Table II.

Development of Disposable Viscometer for Sulphlex

It is quite difficult to clean the viscometers used to measure the viscosity of the Sulphlex because of the poor solubility of the Sulphlex in convenient solvents. We therefore developed a disposable viscometer which consisted of a test tube and a piece of glass tubing. The bore of any one long piece of glass tubing is precise enough so that the viscosity of a known standard may be run in one section to calibrate the others.

The test method used is essentially that described in ASTM test method D-2171, with the viscometer used considered to be a modification of the modified Koppers viscometer described in that method. The viscometer is shown in detail in Figure 3.

In this method, a four foot length of glass tube is cut into six pieces and each piece is marked off as is shown in Figure 3. The glass tube is inserted into the test tube so that the first mark is exactly 3 inches above the bottom of the tube. Exactly two inches of asphalt or Sulphlex are placed into the test tube, then the glass tube reinserted. (The asphalt or Sulphlex will raise a bit, but all will be identical.) Vacuum is applied and the time required for the passage of the miniscus through each segment is determined. The times are recorded for duplicate samples of an asphalt for which the viscosity is known, and calibration constants are determined for the other four tubes of the set.

Once the capillary tubes are used, they are discarded. The test tubes may be cleaned by first soaking them in asphalt or an aromatic oil, then cleaning them with trichlorethylene.

Data obtained on three samples of Sulphlex are shown in Table III.

Emulsion Formulation Studies

Evaluation of Standard Asphalt Formulations

The first step in developing emulsions from the sulfur extended asphalt (SEA) and Sulphlex base stocks was to determine whether standard emulsion formulations might work. We found out quite early that generally standard formulations would not work. We also found that we were working with three, not two, different types of base stocks; SEAs in which the sulfur is dissolved in the asphalt (10 and 15% sulfur) SEAs in which part of the sulfur is dissolved and part dispersed (30 and 40% sulfur) and the Sulphlex base stock.

Satisfactory anionic emulsions could be readily prepared at 10 and 15% if the emulsifier was increased, however considerable difficulty was encountered in making any of the other emulsions. Our initial attempts to make emulsions from the Sulphlex base stock were miserable failures. In our first attempt, the emulsion broke in the mill and lines, causing quite a mess. Latter attempts were successfull, however.

Formulation Considerations

Emulsions are a dispersion of one material in another with a third component that establishes itself at the interface of the two incompatable phases. The two phases we are concerned with are the base stock (SEA or Sulphlex) and water, and the third component is a chemical (as opposed to a finely divided particulate). For an emulsion to be formed, one part of that chemical (the emulsifier) must be soluble in one phase while another part of the emulsifier must be soluble in the other phase. The continous phase is usually that which has the greatest affinity for whichever part of the chemical. Thus, if the water soluble part of the emulsifier is more strongly dissolved in water than is the "oil"* soluble part soluble in the "oil", the emulsion will be Oil in Water (O/W).

If, on the other hand, the oil solubility is stronger, the emulsion will be Water in Oil (W/O). It is possible to make emulsions at one temperature in which O/W prevails only to have them invert to W/O when the temperature is changed, or the electrolyte is changed. As examples, an O/W emulsion based upon Sodium Stearate can be inverted by cooling the emulsion. Likewise, emulsions prepared at lower temperatures $(70-120^{\circ}F)$ with certain exthoxylated emulsifiers may be inverted by increasing the temperature. Other factors may cause inversion including adding multivalent ions (to anionic emulsions) adding sodium ions to certain sodium soaps (salting out of the soap), increasing the phase volume of the dispersed phase, etc. For an emulsifier to work, it must partition itself at the interface. If it cannot do this, it won't work.

Our tasks in making satisfactory emulsions included finding materials which would act as emulsifiers for the sulfur containing base stocks, and finding ways by which the rate of settlement of the particles could be reduced. This settlement problem was a result of the higher specific gravity of the sulfur containing base stocks.

*"Oil" in this case to include SEA on Sulphlex base stocks.

Sulfur, being similar to oxygen, is a very reactive element. In nature it occurs as a polymer containing eight sulfur atoms per molecule. Light can cause the S-S bond to break, ⁵⁾ activating the sulfur to react, although in the black world of asphalt, light would not be expected to be a problem. Bateman et al ⁶⁾ have shown that the S-S bond is readily broken by nucleophilic reagents such as SO₃, CN⁻, RS⁻or HS⁻⁷⁾⁸). There is also evidence that R₃N: and R₃ P: nucleophides will cause chain sission ⁹⁻¹¹). Thus the cationic emulsifiers, being amines, may very well caty-lize the sission of the S-S bond and accelerate the reaction of sulfur with asphalt.

We have noticed a strong odor of ${\rm H_2S}$ in emulsions, even though the sulfur is added just prior to emulsification.

The reaction has been suggested to be;

$A-S-S-B+R_3N$ R_3N+AS^+SB

This could be the reaction with additives such as Redicote AP, however the emulsifier amine carries a positive charge, thus it is not the same. There are amines in asphalt, however which might enter into some reaction.

Batman et al^{6} have discussed the interaction of the S-S bond with olefinic double bonds. The electron doner activity of the olefinic bond will promote polarization of the S-S bond and then attachment at the double bond.

Ross 12) has studied the kinetics of the reaction of sulfur with cyclohexene and other olefins at $110-140^{\circ}$ C and has found the reaction to be autocatalytic and that in the early stages the rate is proportional to the square root of the sulfur, olefin and product concentrations. This is in agreement with Ludwig 2, who found that adding previously reacted Sulphlex to a new batch being prepared markedly increased the reaction rate.

It is quite evident from this very brief discussion that the interaction of sulfur with the asphalt and emulsifiers may be quite involved. We know from experience that air blowing asphalt reduces its desirability as an emulsion base stock. One might expect that sulfurization of asphalt might also be detrimental to emulsion quality.

Use of Multifunctional Emulsifiers

One of the causes of problems with stability of the sulfur containing base stocks might be lower solubility of the "oil" soluble moiety of the emulsifier in the sulfur containing oil. It appears that this might be progressive, occurring after an emulsion has been made. Since sulfur will react with amines, we felt that adding an aminated ethoxylate might provide us with a way to obtain an emulsifier which would have an adequately oil soluble radical. To evaluate this, we obtained some samples of an ethoxylated tallow amine, an ethoxylated oleyl amine and a coco sulfobetaine from Sherex Chemical Company. We made cationic emulsions of the first two and an anionic emulsion with the latter one. The cationic emulsions failed quite soon after being made, however the latter one tid not look bad, although reversible agglomeration had occurred. he base stock was Sulphlex.

"se of Unsaturated Fatty Acids

n discussing our problem with Dr. Michael Raymont¹³) it appeared that molecules with double bonds might be caused to react with fulfur. If such a material also had a water soluble or potentially ater soluble group which might not react with the sulfur, it might be possible to produce stable emulsions by pre-reacting the sulfur or Sulphlex with that material, then making an emulsion. Our first experiment was attempted with the aid of Dr. Brian Collar at the federal Highway Administration Laboratory. We found that reacting Sulphlex with oleic acid at about 275° F for an hour would allow us to produce satisfactory emulsions of the Sulphlex base asphalt.

Continuing along that line of experimentation, we obtained several mixtures of oleic acid and linoleic acid and found them to be quite effective. The most effective of those which we tried was PAMAK #CFA (Western Crude Fatty Acid) made by Hercules. The concept which worked for Sulphlex worked equally well for the SEA base stocks. We also found that reacting the PAMAK WCFA with sulfur containing base stocks also greatly improved the quality of cationic emulsions as well as anionic emulsions.

Effect of a Protective Colloid

One of the methods of reducing the settlement of an emulsion or dispersion is to increase the viscosity of the continuous phase. According to Stokes 14), the rate of settlement or "downward creaming" is directly proportional to the square of the radius of the particle, directly proportional to the difference in specific gravities and inversely proportional to the viscosity of the continuous phase (with the assumption that the dispersed phase is rigid. If the dispersed phase is deformable, the rate of settlement will be greater). Thus adding materials which increase the viscosity of the aqueous phase should reduce the settlement. Although we have obtained about 25 different samples of protective colloids which might increase the viscosity, only one was evaluated, as it worked very well. It was outside of the scope of this investigation to evaluate all 25. The protective colloid used was Natrosol 250HR, made by Hercules, which is widely used by the paint industry.

By reducing the rate of movement of the particles, the chance of coalescence of the particles is reduced thus providing an increase in emulsion stability (as defined as decreased rate of coalescense) as a by-product.

Effect of Redicote AP

We wish to consider Redicote AP (ARMAK) separately from other additives, as it appears to provide some beneficial effect, although the extent is not quite clear. Redicote AP is used as an additive to asphalt to improve the ameneability of that asphalt to be emulsified. ARMAK recommends that it be added to asphalt and be allowed to cure for several hours prior to emulsifying the asphalt. As it is heat stable, and is an amine, we felt that it might react with the sulfur, providing a system which would be more ameneable to emulsification. Although our data did not clearly show a beneficial effect by itself, the data do suggest that the use of Redicote AP in conjunction with PAMAK WCFA may have a dramatic effect. As the experiment, which will be discussed later, confound that interaction with other interactions, it is not clear that the effect was real. Since the Redicote AP is a base, and readily soluble in asphalt, and the PAMAK WCFA is an acid, the sulfur reaction product most probably is soluble in sulfur (since certain of the Sulphlex formulations were based upon crude tall oil pitch²), they would react, and possibly aid the primary emulsifiers in producing an emulsion. We have found that adding the anionic emulsifier PAMAK WCFA to cationic systems appears to improve the emulsions. Likewise, the data suggest that the presence of Redicote AP in cationic and anionic systems might be quite beneficial. The data are not clear, and it is outside of the scope of this project to follow that line of experimentation to obtain specific effects of organic acid-base reaction products on emulsion quality.

Effect of Reaction Conditions of the Sulfur, PAMAK WCFA and Asphalt

on Emulsion Quality

The questions arose as to the best method by which to react the PAMAK WCFA with the sulfur, the effect of temperature and the effect of length of reaction time. Although we could not completely separate these effects, we did arrive at some definite conclusions.

Effect of Time. The longer the sulfur and PAMAK WCFA are reacted together, the better the emulsion. Although we limited the reaction time to 2 hours, our data definitely indicated that the longer the PAMAK WCFA was reacted with the sulfur, the better the emulsion. 2 hours was definitely better than ½ hour, and reacting them overnight was definitely better than 2 hours. We arbitrarily settled on 3% PAMAK WCFA, based on sulfur, for the amount used, although the data did not show any particular trend with respect to the amount of PAMAK WCFA. It is insoluble in sulfur. We mix them together with strong stirring for the desired period.

Effect of Temperature. One would expect that the reaction rate would increase exponentially with temperature. We were not able to get a clear picture, although the only experiment tried was to compare the effect of temperature of curing of a mixture of sulfur, PAMAK WCFA and asphalt on emulsion quality. No clear trend appeared. As we know that oxidation (air blowing) reduces the quality of an emulsion base stock, and sulfur reacts with asphalt in a manner similar to oxygen, the experiment may have been confounded by the presence of the asphalt. Although we cannot include in the scope of this project a study of the reaction kinetics of sulfur and unsaturated fatty acids, it would be very interesting to determine if reacting them at a higher temperature in the absence of asphalt would be beneficial.

Effect of the Presence of Asphalt. PAMAK WCFA is quite soluble in asphalt, as is sulfur at levels less than about 20%. It would be much more convenient, both in the laboratory, and commercially if the reaction could take place in such a blend. Although emulsions made with such blends were better than emulsions made with uncured base stocks, the presence of the asphalt was detrimental. Considerably better emulsions were prepared when the PAMAK WCFA and sulfur were reacted separately, then added to the asphalt than when asphalt was present during the curing.

Effect of "In Situ" Neutralization of the Emulsifiers. As was mentioned above, the rate of settlement of emulsion particles is directly proportional to the square of the particle size. Thus, a reduction in particle size to, say, ' of the original size will decrease the rate by a factor of four. The method generally used to make emulsions is brute force, ie, the oil phase is placed into a high shear field which physically reduces the size of the emulsion particles. Another method of making emulsions is "persuasion", ie, the emulsion is "persuaded" to form by the thermodynamics of the system. As an example, one way to make an oil in water emulsion is to add a fatty acid, such as oleic acid, to the oil, then slowly add a caustic soda solution. A W/O emulsion is first formed, as the caustic reacts in situ with the fatty acid, because of the very high volume of the oil phase. At some point, when the aqueous phase volume is high enough, the emulsion inverts, forming a stable O/W emulsion. This technique cannot be used in asphalt emulsions or those made with SEA or Sulphlex base stocks because water boils at a temperature much lower than the temperature of the oil phase. It is possible to take advantage of the thermodynamic energy from in situ neutralization, however.

By adding a free acid (such as PAMAK WCFA when used as an emulsifier or Vinsol resin) to the oil phase prior to making the emulsion, then milling that oil phase with a caustic soda solution, we can get a combined effect of the "brute force" and "persuasion" techniques. We found that emulsions made in that manner were of superior quality to those made neutralizing the emulsifier in the aqueous phase prior to making the emulsion.

As sulfur reacts quite rapidly with amines, we were not able to demonstrate the above with cationic emulsions.

Factorial Designed Experiments.

In research or development projects in which there are many variables, some of which interact, it is extremely difficult to determine the real effects of a variable and to determine whether there are interactions if experimental techniques are used in which one variable is changed while the others remain constant.

A factorial designed experiment, on the other hand, provides information concerning effects and interactions. It is also possible to add additional variables by "confounding" the effect of a variable with interactions, although precision is reduced. The factorial designed experiment is much more efficient than that of varying one variable at a time. Another disadvantage besides lack of efficiency of a single variable experimental technique can be that of calculating the regression equation, unless a computer is available, because of the difficulty of inverting the experimental matrix to obtain the regression coefficients. Care is taken with the factorial experiment so that regression coefficients are readily calculated.

Theoretical. The factorial designed experiments of interest in this study are those with variables (or treatments) entered at two levels. They are designated as 2^n factorial designed experiments. For a full replicate, 2^n experiments are needed. Two levels of each variable are selected, close enough to each other so that their response may be considered linear, and monotonic. Each treatment is transformed according to the equation:

$$a = \frac{2x - x_2 - x_1}{x_2 - x_1}$$

where a= transformed variable, an integer
 X= treatment

 $\begin{array}{l} x_{2} \neq \text{ high level} \\ x_{1} = 1 \text{ ow level} \\ \therefore \quad a \in E_{1,2} \neq 1 \end{array}$

The experiments are then carried out at each permutation of the two levels. As an example, a 2^3 experiment would include the following eight sets of treatments.

Experiment Treatments

	A	B	С
-	-1	-1	-1
a	+1	-1	-1
ь	-1	+1	-1
ab	+1	+1	-1
С	-1	-1	+1
ac	+1	-1	+1
bc	-1	+1	+1
ahc	+1	+1	+1

From this experiment, we can assess the effect of the three treatments, and their interactions. Evaluation of the data from these eight experiments will provide the regression coefficients for the three treatments and interactions. These experiments may be replicated for error assessment, experiments in replicate may be run at the center point of the design (0,0,0) or, if certain of the re-gression coefficients are small in comparison to other effects, they may be used to estimate error (which they will usually overestimate). In addition, if the interactions are small, it is possible to enter an additional variable in place of an interaction. To do this, one makes a defined contrast on one of the interactions (separating the negatives from the positives). As an example, if a defined contrast is made on the abc interaction, four experiments would be required to assess the effect of the three variables (assuming of course that the magnitude of the error is known). In the following table is shown such a defined contrast (the ls are eliminated for convenience).

Experiment	Treatment							
	м	A	в	AB	с	AC	BC	ABC
Θ	+	-	-	+.	-	+	+	-
a	+	+	-	-	-	-	+	+
b	+	-	+	-	-	+	-	+
ad	+	+	+	+	-	-	-'	-
c	+	-	-	+	+	-	-	+
(aC)	+	÷	-	-	+	+	-	-
õ	+	-	+	-	+		+	-
abc	+	+	+	+	+	+	+	+

Those circled are selected for the defined contrast. Note that the variable a is confounded with -bc, b is confounded with -ac and c is confounded with -ab, that is, one cannot tell the difference between b and -ac, a and -bc and c and -ab. We are assuming that the interactions are quite small in comparison with the main effects. This 2^3 , 1/2 replicate experiment is designated 2^{3-1} .

The experimental design as shown is selected for reasons of geo-The experimental design as shown is selected for reasons of geo-metry which will greatly aid in evaluating the experiment. First of all, all columns vectors, X_1 of X, the experimental matrix are orthognal, that is, the vector product $X_1, X_2 = 0$, $x \neq 1$ The re-gression equation is $Y = X O + \varepsilon$ where $\varepsilon = \operatorname{error}$ and Y = X O is the least squares estimator, Y is the matrix of observed data and X is the MXM design matrix, where $M = 2 n^{-C}$; n = the number of treatments, and C = 0 for a full replicate, 1 for 1/2 replicate, 2 for 1/4 replicate, etc.

 $oldsymbol{eta}$ are the least squares estimator for the experiment. This equation can be rearranged to

$$\hat{\beta} = (\mathbf{X}^{\mathsf{T}} \mathbf{X})^{\mathsf{T}} \mathbf{X}^{\mathsf{T}}$$

X' = transpose of X

This particular type of design results in $\mathbf{X}^T \mathbf{X} = \mathbf{m} \mathbf{I}$ where X; EX , 2 = 1,2 ... m ,

I = Identity matrix

Thus $(\mathbf{X}^{\mathsf{T}}\mathbf{X})^{-l} = \frac{1}{m} \mathbf{I}$ and $\therefore \hat{\beta} = \pm I \times^{\mathsf{T}} \mathsf{Y}$

 \widehat{eta}_i is the mean while the other $\widehat{eta}_j, i
eq j$ represent the deviation from the mean.

If one finds that many of the β_{λ} values are small, with only a few that appear to be of significance, those which are small may be used as an estimate of the error. Replicate experiments at the mid point of the experiment $(0,0,\ldots,0)$ may be run to obtain an independent estimate of error. The total sum of squares is given by

 $ss_{\tau} = \mathbf{y}' \mathbf{y}$

and that from regression;

$ss_{Reg} = \beta^{T} \mathbf{X}^{T} \mathbf{X} \beta^{T}$ $= \beta^{T} (m \mathbf{I}) \beta^{T}$

error of course is

$$SS_E = SS_T - SS_{Reg}$$

In our studies, the matrix β was separated into two matrices; β , φ

 β_2 such that β_1 included those which were felt to be significant while those of β_1 were used for error. SS_{Req} then became

$$SS_{reg} = \beta_i^{T} (m I) \beta_i$$

Either the t test or F test may be used to establish significances.

CSS Emulsion. 30 and 40% Sulfur in SEA. A 2^6 , 1/4 replicate factorial designed experiment was carried out using as variables those shown in Table IV. The variables used were % sulfur (a), reaction time of PAMAK WCFA and sulfur (b), % Indulin W-3 (c), % Natrosol (d), % Redicote AP (e), and % PAMAK WCFA (f). The interactions between the % Indulin W-3 and reaction time, and % Natrosol 250HR and reaction time were considered to be quite small, thus the % Redicote AP was confounded with the bc interaction and the % PAMAK WCFA was confounded with the bd interaction. The results are shown in Tables V and VI. The experiments shown are as if the experiment was a 2^4 full replicate, and e and f were interactions. This was done for convenience because of the length of time required to define each of the four effects of interactions which are confounded. Increasing the sulfur caused the quality to decrease but had only a slight effect (within experimental error) on the % solid and viscosity. Increasing the reaction time with the PAMAK WCFA and the sulfur made a marked increase in quality, viscosity and solids. There seemed to be a mild interaction between those two variables with respect to solids and viscosity. Increasing the Indulin W-3 increased viscosity, but otherwise had little effect. The Redicote AP appeared to have little effect by itself, although it might be interacting. With the level of confounding in this experiment, it is not possible to establish for sure what has occurred on the in-teraction term labeled bcd. The Natrosol appeared to improve quality and decrease solids. That decrease in solids is probably related to the increased viscosity of the soap solution which results in an increased pump rate for the feed pump. The PAMAK appeared to increase solids and decrease the viscosity.

None of these emulsions were of suitable quality, however the information obtained suggests directions of future study. <u>SS Emulsion.</u> <u>30 and 40% Sulfur in SEA.</u> A 2^5 , one half replicate factorial designed experiment was carried out with % sulfur (a), cure temperature (b), mill setting* (c), % Vinsol (d) and % Redicote AP (f) as the variables. The curing system for the sulfur consisted of adding 3% PAMAK WCFA (based on sulfur) into a mixture of asphalt and sulfur and curing them for 2 hours at the temperatures selected in the design.

The variables are as follows:

a.	Sulfur	30, 40% (based on base stock)
b.	Cure tem.	280, 310 [°] F
c.	Solids	approx. 55 & 60 (based on mill settings)
đ.	Vinsol NVX	1.0, 1.6
e.	Redicote AP	0, 0.2 (based on base stock)

A defined contrast was made on the abcde interaction, which resulted in the confounding of certain effects and interaction. Following is a list of the effects and interactions which are confounded with each other ($a \equiv -bcde$ means that the effect a is confounded with the negative of the bcde interaction.)

m _≡ -abcde	d ≡ -abce	bc ≡ -ade	ae Ξ -bcd
a _∃ -bcde	e ≡ -abcd	ad Ξ - bce	be \equiv -acd
b <u>≡</u> -acde	ab ≡ ~c de	bd ≘ -ace	ce ≡ -abd
c ≝ -abde	ac Ξ -bde	cd = -abe	de = -abc

(the negatives occur because the negative defined contrast was used).

Four replicate experiments were run at the center point of a=35, b=297 (mean of the log of the obsolute temperatures), c=57.5, d=(mid level) and e=0.1 to estimate error and possible detect curvature.

Since only four emulsions can be made a day, the experiment was set up with four blocks of four runs each plus the replicate block. The effect of the blocks are confounded with the mill setting (solids, (c)) and % Redicote AP (e). The mill setting was used as one because we felt that attempting to change the mill (ie., pump rate for asphalt) each time would cause more error than running two blocks at one setting, the mid point block at another, and then two blocks at still another setting. The effect of the Redicote AP is unknown, but we would rather have its effect confounded with the blocks than either of the other three.

The experimental design and transform equations are shown in Table VII. The data gathered included & solids, Brockfield viscosity at different times after manufacture and settlement evaluation. Two methods were used to assess settlement. Duplicate test tubes were set up with each emulsion and the settlement was followed with time as evidenced by the formation of a dark liquid on top. A subjective evaluation was also made by allowing the emulsions to set for a week and then estimating the seriousness of the settlement as evidenced by thick emulsion on the bottom of the container. For the most part, the error was assessed by using effects and interactions which appeared small compared to others, then evaluating the significance of the apparently real effects using the t test. Increasing the sulfur content tended to decrease the viscosity as did increasing the cure temperature. Increasing the mill setting (increased solids) had a marked effect on viscosity, as would be expected. The effect of increased emulsifier content was below the 90% confidence limit while the addition of the Redicote AP appeared to cause an increase in viscosity.

* Defined as speed of asphalt pump to mill.
Three interactions appear to be significant; that between the % sulfur and mill setting, that between the cure temperature and mill setting and that between the % sulfur and % emulsifier. The first two caused a decrease in viscosity while the last caused an increase. Tables VIII and IX detail the analysis of variance.

The effect on quality is difficult to assess. With respect to overall settling, as evidenced by the appearance of a dark liquid on top of the test tube samples, the variable which had the greatest effect was the mill setting, which is understandable. The faster the asphalt pump turns, the higher the solids and the lower the amount of free liquid available. On the other hand, increasing the solids appeared to cause more material to settle to the bottom as evidenced by the subjective estimation when the samples are stirred.

Since bottom settlement is not necessarily related to inverse creaming (free liquid at the top), these effects may be real. With the high potential error in the subjective assessment, the conclusions should be used advisedly.

Mixes With Aggregate

Some mixes were prepared with slurry seal aggregate, and with chip seal aggregate with results which one would expect with the type of emulsifier used, with the exception that RS and CRS emulsion with high amounts of emulsifier would mix better than one would have otherwise expected.

Details of Emulsion Formulations

Introduction

In the following sections are described the emulsions which were attempted. In the tables showing the formulations, the amount of sodium hydroxide or hydrochloric acid used is not shown as sufficient was used to arrive at the desired pH. When organic acids or bases are added to the oil phase, sufficient base or acid is added to the aqueous phase to neutralize them and obtain the desired pH. This is arrived at either by calculating the amount needed from the structural formula or measuring it directly by titration prior to formulating the emulsions.

The stability of the emulsions were hoted immediately at the mill, 24 hours later then a few days later. Emulsions which settled but could be remixed were considered to be good.

The emulsions are divided up as to emulsifier type; anionic slow set, anionic rapid set, cationic slow set, cationic quick set and cationic rapid set. The classifications are based upon what one might expect if asphalt was the base stock. In general, the presence of sulfur tended to reduce the stability, thus an emulsion made with slow set emulsifiers and the SEA base stocks or Sulphlex would tend toward acting more like a medium set emulsion. As it was necessary to react the sulfur or Sulphlex with PAMAK WCFA, a tall oil, before making the emulsions, and sometimes adding it also to the asphalt, normally slow set emulsions would be quickened as PAMAK WCFA is a rapid set emulsifier.

Emulsions from 10% SEA. Slow Set. In Table X, are shown the SS type emulsions which were prepared. All were based upon Vinsol NVX (Hercules) as the prime emulsifiers with the lignosulfonate stabilizers Orzan A and Marasperse CE.

All trials made emulsions which were quite good, however settlement did occur. As the Vinsol NVX concentration was increased, the amount of settlement decreased. The addition of Natrosol 250HR markedly improved the emulsions. An experiment was tried to determine whether adding the Vinsol to the asphalt prior to making the emulsion, and curing the asphalt sulfur mixture in the presence of the Vinsol would be beneficial. We had found that such procedures were very helpful in making RS emulsions. Trials 25-14A, 15A and 15B were involved in that study. We found that the best emulsion was that in which the emulsifier was in the aqueous phase, and that the longer the sulfur was in contact with the emulsifier-asphalt blend, the poorer the emulsions. All three were adequate emulsions, however.

Our recommended formulation for a 10% SEA emulsion is:

2% Vinsol NVX (on total) 0.7 Marasperse CE 0.1-0.15% Natrosol 250HR

Emulsions From 10% SEA. Rapid Set. The 10% SEA rapid set emulsions were quite easy to make using PAMAK WCFA, especially if the FAMAK WCFA is first added to the asphalt sulfur blend, and the blend allowed to react. For that reason, most research which would be applicable to the 10% SEA emulsions were done on 15% SEA emulsions. If one can produce stable 15% SEA emulsions, there would be no difficulty in producing 10% SEA emulsions. The data are shown in Table XI.

Adding the emulsifier to the blend of asphalt and sulfur and allowing them to cure for two hours greatly improved the emulsions. The addition of Natrosol 250HR also was quite beneficial. The recommended formulation is as follows, based on total:

> 0.5-0.75% PAMAK WCFA (added to asphalt) 0.3% PAMAK WCFA, added to the sulfur 0.15-0.25 Natrosol WCFA

Emulsions of 10% SEA Base Stocks. Cationic Slow Set. The data

on the emulsions prepared are shown in Table XII. The emulsifiers which appeared to work best was Indulin W-3, although, when used by itself, did not perform exceptionally well. Increasing the emulsifier content and adding Natrosol 250HR improved the performance of the Indulin W-3.

Adding 3% PAMAK WCFA to the sulfur prior to adding the sulfur to the asphalt allowed the amount of emulsifier to be reduced, and excellent emulsions were produced. They remained stable, with only slight settlement for at least a couple of weeks.

More effort has been placed upon emulsions containing 15% or more sulfur as any formulation which will produce good emulsions at 15% sulfur in the SEA base stock will produce good emulsions with 10% SEA base stocks. There is some evidence that the longer the PAMAK WCFA cooks with the sulfur, the better the emulsion. Emulsion 25-17B had less settlement after a couple of weeks than did emulsion 25-17A.

A formula which was found to work quite well was one containing the following ingredients, based on total emulsion:

0.065% Natrosol 250HR 2.0% Indulín W-3 0.2% PAMAK W-3 (3% based in sulfur) added to the sulfur and cured for 2 hours.

The significant effects were the benefits of adding the Natrosol 250HR and the improvements that occurred from reacting PAMAK W-3 with the sulfur prior to adding the sulfur.

Emulsions of 10% SEA Base Stocks. CQS. Only three emulsions were tried and they were failures. The data are shown in Table XIII.

Emulsions of 10% SEA Base Stocks. CRS. Most of our work has been done with 15% SEA base stocks since any formulation which will make emulsions from that base stock will surely make them with 10% SEA base stocks. Conclusions gained are that increasing the emulsifier produces an improved emulsion, adding the Natrosol 250HR improves the emulsion while decreasing the solids improves the emulsion. There are other influencial factors such as adding PAMAK-WCFA and Redicote AP, however those experiments were done with the 15% SEA base stock. We did evaluate the effect of using FeC13 as an acid in place of HC1. The thought being that the Fe⁺⁺⁺ ion could pick up the sulfide and reduce the H₂S odor. No great effect was found, and it appeared that the emulsion in which HC1 was used was superior. The data are shown in Table XIV. The formula which was used for the 5 gallon sample was:

1.5% ARMAK E-67 0.065% Natrosol 250HR

Emulsions of 15% SEA Base Stocks. SS Types. In Table XV are shown the emulsions evaluated in this series. Very satisfactory emulsions could be made using Vinsol NVX and Marasperse CE. Superior emulsions can be made when Natrosol 250HR is also added. The following formulation is the optimum one at this time:

> 1.8-2.2% Vinsol NVX 0.6-0.08% Marasperse CE 0.06-0.08% Natrosol 250HR

Emulsions of 15% SEA Base Stocks RS Type. In Table XVI are shown the emulsions evaluated in this series. While we were able to obtain satisfactory emulsions using solutions of neutralized PAMAK 4 and PAMAK WCFA, at 2% (based on total emulsion) we obtained superior results at half the level of emulsifier by reacting that plus 0.7% more PAMAK WCFA to the asphalt and forming the scap in situ. Caustic soda is placed in the aqueous phase which then reacts with the PAMAK WCFA during emulsification. Our preferred formulation based upon total, is:

> 0.3% PAMAK WCFA in sulfur, 2 hr. cure @275°F 0.7% PAMAK WCFA in asphalt as free acid 0.07% Natrosol 250HR in NaOH solution

Emulsions of 15% SEA Base Stocks, Cationic Slow Set. In Table XVIII are shown the data for the CSS type emulsions for the 15% SEA base stocks. As may be seen, we have had great difficulty in finding formulations which will provide satisfactory emulsions. The only truly successful CSS emulsion had 2.0% Indulin W-3, 0.5 Recicote AP and 1.8% PAMAK WCFA, based on total emulsion. That amount of emulsifier may be too much to be econimically sound, however, in our frustrations, we wished to have at least one successful emulsion. We therefore boosted the emulsifier and tried every trick we had to produce a satisfactory emulsion. Experiments 25-19A & B and experiments 25-46L 15, 16 and 25-47L 3 and 5 all demonstrate that it is important to react the PAMAK WCFA with the sulfur prior to adding it to the asphalt, and suggests that the Redicote AP may be providing a benefit. Note that the addition of the anionic emulsifier PAMAK WCFA to the cationic emulsion system markedly improves quality. The only successful formula at this time is as follows:

 Indulin W-3 (100% active)
 2.7% on total

 (7.7%, 35% active)

 Redicote AP
 0.5

 PAMAK WCFA
 1.8

 Natrosol 250HR
 0.1

The Natrosol is added to the aqueous phase with the Indulin W-3 and the pH is lowered to 1.5. 3% PAMAK WCFA (on sulfur) is added to the sulfur and cured for at least 2 hours at 275° F. 3% PAMAK and 0.8% Redicote AP (based on asphalt) are added to the asphalt and just prior to emulsifying the reacted sulfur -PAMAK WCFA mixture is added. The emulsion is then made.

Emulsions of 15% SEA Base Stocks. Cationic Rapid Set. The results of our attempts to make a satisfactory CRS emulsion using the 15% SEA are shown in Table XVIII. As may be seen, all results were dismal failures except the one into which we reacted the sulfur with PAMAK WCFA and also added the PAMAK WCFA into the asphalt. We went high on the emulsifier as the PAMAK WCFA into the asphalt. We went high on the emulsifier as the PAMAK and E-67 would be expected to react with each other, perhaps providing a benefit but reducing the amount of emulsifier available. That emulsion was excellent and remained that way. Further work might show that the emulsifier level could be reduced, however at this point, our recommended formula is as follows, based on total emulsion:

Redicote	E-67	2.0
Natrosol	250HR	0.06
РАМАК WCH	A	0.62

3% PAMAK WCFA (based on sulfur) is reacted with the sulfur for a minimum of 2 hours, then added to the asphalt to which 1% (based on asphalt) PAMAK WCFA had been added. The emulsions was then immediately made.

The chemistry of the interaction of organic acids and bases in these emulsions are intriguing as one would expect that such reaction products might harm the emulsion. On the contrary, the emulsion was aided.

Emulsions of 30 and 40% SEA Base Stocks. Slow Set. Data on the emulsions prepared with SEA base stocks containing 30 and 40% sulfur are shown in Table XIX. As may be seen, many potentially satisfactory emulsions were prepared. Many of these emulsions were discussed earlier under "SS Emulsion. 30 and 40% Sulfur in SEA" in the section on factorial designed experiments. Successful emulsions required the reaction of PAMAK WCFA with the sulfur for at least two hours. We also found that better emulsions were formed if PAMAK was also added to the asphalt. The presence of PAMAK WCFA in the SS formulation makes the emulsion tend more towards an MS emulsion than an SS.

The optimum formulations which we have at this time are as follows, based on total emulsion:

		· <u> </u>
	30%	40%
Vinsol NVX	2.5	2.88
Marasperse CE		0.8
PAMAK WCFA - in sulfur	0.54	0.72
PAMAK WCFA - in asphalt	0.84	-

The PAMAK WCFA is reacted with the sulfur for a minimum of 2 hours, then added to the asphalt just prior to making the emulsion. If PAMAK WCFA is added to the asphalt, it is introduced prior to adding the sulfur. Emulsions of 30 and 40% SEA Base Stocks. Rapid Set. Very few emulsions were run to obtain successful emulsions based upon SEA base stocks containing 30 and 40% sulfur, as may be seen in Table XX. That was a result of what was learned with formulation of the other emulsions. The anionic rapid set emulsions were the easiest to formulate as long as part of the emulsifier was reacted with the sulfur before making the emulsion. The formulations which we felt were optimum at this time are those shown below. The formulations are based upon total emulsion.

	<u> </u>	SEA
	30%	403
PAMAK WCFA in sulfur in asphalt	0.54 1.50	0.74 2.40
Natrosol 250HR	0.075	0.06

The sulfur and PAMAK WCFA were reacted for at least 2 hours before adding them to the blend of asphalt and the remaining PAMAK WCFA.

Emulsions from 30 and 40% SEA Base Stocks. Cationic Slow Set. The data obtained are shown in Table XXI. As may be seen, adequate formulations for CSS emulsions were not attained, although one formulation appeared fair, based upon the 30% SEA base stock. That formula had as additives PAMAK WCFA and Redicote AP, which appeared to materially improve the emulsion. The multitude of variables make it very difficult to ascertain trends, which was the reason the factorial designed experiment was done. In that series, the PAMAK WCFA and Redicote AP were first added to the asphalt, cured for 2 hours, then the sulfur was added and cured for 15 or 120 minutes as designated in the design. Later work has shown that the PAMAK WCFA should be cured with the sulfur before the sulfur is added to the asphalt rather than cured in the presence of the asphalt as was done in the factorial experiment (which has been discussed in detail in the "Factorial Design" section).

Another variable which was not evaluated was the effect of the reaction of the PAMAK WCFA and Redicote AP, which undoubtably took place in the asphalt and which was apparently beneficial.

Although we have not been successful in formulating a CSS emulsion based on the 30 and 40% SEA base stocks, there are promising trends, although those trends cannot be followed at this time. A factorial design with % sulfur in the SEA, % PAMAK WCFA in the sulfur, % PAMAK in the asphalt and % Redicote AP in the asphalt as variables with cure time held constant would tell us if these emulsions could indeed be made.

All emulsions save one, were bad, as was mentioned above. The Indulin W-3 emulsions, in general, were "less bad" than were those emulsions in which other emulsifiers were used. This was also found to be true with emulsions with lower percentages of sulfur. Emulsions from 30 and 40% SEA Base Stocks. Cationic Rapid Set. Only one CRS emulsion was attempted with the 40% SEA base stock and none with the 30% SEA base stock. None had been attempted because we had not, until quite recently, had success with the CRS emulsions made with SEA base stocks with lower concentrations of sulfur. The emulsion was attempted (#25-5B) on a 40% SEA base stock to which was added 1% Redicote AP (based on oil phase) with an emulsifier solution consisting of 2% Redicote E-67 and 0.2% Natrosol 250HR, based on total emulsion. We had hoped that the Redicote AP would have the same effect on cationic emulsions as the PAMAK WCFA had on anionic; we had not yet discovered the extremely beneficial effect of the PAMAK WCFA on cationic emulsions. The emulsion made fine, and had a solids of 51.5%. It completely solidified that same day.

There is again an opportunity for a factorial designed experiment to evaluate the emulsifiers and procedures needed to obtain an adequate emulsion. The variables might be, % Redicote E-67 in aqueous phase, % Redicote AP in asphalt, % PAMAK WCFA in asphalt, % PAMAK WCFA in the sulfur, and % sulfur.

Emulsions of Sulphlex. Since we had such a limited supply of the Sulphlex, most formulation work was done on the SEA base stocks, as we considered that the basic principals involved would pertain to both SEA and the Sulphlex base stocks. The data are shown in Table XXII. As may be seen, adding the PAMAK WCFA to the Sulphlex greatly aided in making anionic emulsions, however adding amine type un-neutralized emulsifiers to the Sulphlex did not generally aid in making cationic emulsions. Adding Redicote AP, however, did appear to help.

As may be seen in the data, clay emulsions based upon Sulphlex turned out quite well. Also, considerable success was found making RS emulsions, and some good CSS and CRS emulsions were also made. We ran out of base stock, thus could not make more emulsions. The key to making Sulphlex emulsions is to react the Sulphlex with tall oil for at least one-two hours prior to making the emulsion.

PROPOSED DIRECTION OF FUTURE WORK

The formulation of emulsions based upon sulfur extended asphalt or Sulphlex turned out to be more than a simple extention of asphalt emulsion technology. The reactivity of sulfur in the SEAs and Sulphlex adds another dimension to these investigations, one which requires some attention to the chemistry of the interaction of sulfur with amines, ethoxylates, unsaturated hydrocarbons, etc. The scope of the project was not broad enough to fully investigate such interactions, or even do an extensive literature search, as we are combining sulfur chemistry with colloidal chemistry (both the dispersion of sulfur in asphalt, and the emulsification of such dispersions). Clearly, with some of the high sulfur SEA base stocks, the sulfur did come out of the asphalt-sulfur dispersion, resulting in clogging of orifices in our mill. Future studies on these systems might include the following areas.

Improving the Dispersion of Sulfur in the Asphalt. A method to obtain a very stable, small particle size dispersion of sulfur in asphalt would be advantageous. Possible methods might include using a static mixer prior to the emulsion mill to blend the sulfur and asphalt, and possibly use the reaction product between the talloilsulfur mixture and the Redicote AP-asphalt mixture to stabilize the dispersion. The syergistic effect between tall oil and Redicote AP might carry over to improving the dispersion. Such studies might evaluate the rate of settlement of high sulfur SEAs with and without these additives. Adding Sulfur as a Separate Dispersion in the SEA Emulsions. Dispersions of sulfur are widely used in rubber latex technology, thus the techniques required to make such dispersions have been worked out. One alternative would therefore be to simply add such dispersions to an asphalt emulsion. An area of study would therefore be to compare SEA emulsions made directly with those made by blending an asphalt emulsion with a sulfur dispersion.

Investigate the Chemistry of the Reaction of Sulfur with Tall Oil and Amines With and Without the Presence of Asphalt. The question has arisen in our minds as to what does the reactions of sulfur with tall oil, amines and asphalt do to the properties of the asphalt. It was outside of the scope of this project to investigate this area, however such chemistry impacts greatly upon emulsion quality. Also, these reactions may very well change the nature of the SEA base stock.

Factorial Designed Experiments for Emulsion Formulation Studies.

This project is ending with still many questions on the formulation variables. As interactions have been discovered, future studies should be layed out as factorial designed experiments to further probe the formulation details.

<u>Clay Emulsions</u>. Several clay emulsions were made with considerable success. A study of clay emulsions of Sulphlex for gasoline proof coatings might indicate considerable success in a use in which there is a great need.

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.



Figure 2. Emulsion Mill #2







Disposable Viscometer

TABLE I.

Effect of Emulsion Distillation on Base Stock Properties

		Initial	After Distillation
10%	s	182	187
15%	s	216	188

TABLE II.

Propertie	es of Asphalt-Sulfur Base Stock	S
Asphalt-U.S.	Oil Co. AR 2000 Emulsion Base	Stock
% Sulfur (weight)	Viscosity @140 ⁰ F, poises	Penetration <u>@77[°]F, dmm</u>
0 10 15 30 50	670.4 384.8 367.1 1) 1)	133 182 216 226 186

 Above about 20% sulfur, the sulfur is no longer soluble. The sulfur separated out and plugged up the viscosity tubes.

	T/	ABLE III.	
Viscosity	of	Sulphlex	Samples

Sulphlex Identification	Viscosity @140°F, poises
#233, #61.5	1443
#233, #60	1432
DCPD	1414

Note: a fourth sample was too soft for the capillary tubes we were using (reportedly about 200 poises). Since the viscosity was already known we did not feel it was the most appropriate use of time to obtain smaller capillaries so run the viscosity.

Experiment			Treatment	ts		
	Sulfur (a)	Reaction Time (b)	Indulin W-3 (c)	% Natrosol (d)	<pre>% Redicote AP</pre>	<pre>% PAMAR final</pre>
-	-1	-1	-1	-1	+1	+1
a	+1	-1	-1	-1	+1	+1
Ъ	-1	+1	-1	-1	-1	-1
ab	+1	+1	· -1	-1	-1	-1
c	-1	-1	+1	-1	-1	+1
ac	+1	-1	+1	-1	-1	+1
bc=e	-1	+1	+1	-1	+1	-1
abc	+1	+1	+1	-1	+1	-1
đ	-1	-1	-1	+1	+1	-1
ad	+1	-1	-1	+1	+1	-1
bd=f	-1	+1	-1	+1	-1	+1
abd	+1	+1	-1	+1	-1	+1
cd	-1	-1	+1	+1	-1	-1
acd	+1	-1	+1	+1	-1	-1
bcd	-1	+1	+1	+1	+1	+1.
abcd	+1	+1	+1	+1	+1	+1

Function

a= <u>\$S-35</u>

 $b = \frac{t-1.125}{0.875}$

TABLE IV. EXPERIMENTAL DESIGN, CSS TYPE 2⁶, 1/4 Replicate Factorial Design

 $c = \frac{(W-3)-25}{5}$ Indulin W-3 (c)²⁾ 20% 30% $d = \frac{N - 0.225}{0.075}$ Natrosol (d) 3) 0.15 0.30 $=\frac{(AP)-0.75}{0.25}$ Redicote AP (e)⁴⁾ 0.5 1.0 PAMAK WCFA (f)⁴⁾ $f = \frac{P-1.5}{0.5}$ 1 2

Treatment Transforms

+1

40%

2.00

-1

30%

0.25

Sulfur(a)¹⁾

Reaction Time,h (b)

% of sulfur in SEA
 % of 35% solution in emulsifier phase
 in emulsifier solution
 on dispersed phase

		TABLE V.	
		DATA MATRIX Y	
		2 ⁶ , 1/4 Replicate	
Experiment	% Solids	Brockfield Viscosity ¹⁾	Order of Quality ²⁾
-	68	4	2
a	70	5	1
b	68	25	14
ab	67	15	8
C	65	11	10
ac	66	9	5
bc=e	68	25	6
abc	70	20	9
đ	43	2	12
ad	67	13	3
bd=f	67	11	15
abd	65	5	13
cd	35	13	7
acd	49	10	4
bcd	65	21	16
abcd	64	18	11

1) Reading, Spindle #5, 50RPM. Measured Immediately after manufacturing.

2) Quality ordering from 1-16, 1=worst and 16=best.

TABLE VI. EFFECT MATRIX B

2⁶, 1/4 Replicate

Experiment	<pre>% Solids</pre>	Brookfield Viscosity	Quality	
	~ ~ ~	10.0	<u> </u>	
nean	62.3	12.9	8.5	
a(sulfur)	4.9*	-2.1*	-3.5	> 99%
b(reaction time)	8.0>95%	s 8.9) 99%	6	> 99%
ab	5.4>90%	-3.9 >95%	1*	
c(Indulin W-3)	-4.1*	5.9 >99%	.0*	
ac	0.9*	1.1*	1*	
bc=e(Redicote AP)	4.1*	1.1*	-2*	
abc	1.9*	3.4 >95%	0.5*	
d(Natrosol)	-10.9>998	s →2.6 >90%	3.25	> 99%
ađ	3.9*	1.9*	-1.25*	
bd=f(PAMAK WCFA)	7.9>95%	t -4.9 ≯99%	1.25*	
abd	-4.9*	-0.38*	0.25*	
cđ	-3.1*	1.9*	-1.25*	
acd	-1.4*	-1.6*	-0.25*	
bcd	13.9>998	≥ 2.6 > 90%	2.75	>95%
abcd	0.9*	1.1*	-2.75	\$95 ر
Mean deviation ¹⁾ Stand. deviation ¹⁾	0.29 3.56	0.38 1.56	-0.075 1.11	
t test				
±90	4.92	2.21	1.53	
±95	6.52	2.95	2.02	
t ₉₉	10.03	4.67	3.12	

* Used for calculating error.

1) Mean deviation and standard deviation of those marked *.

with Quadruplicate Center Point						
Experiment		1	reatments			
	· · · · · · · · · · · · · · · · · · ·		Mill	Vinsol	Redicote AP	
	Sulfur (a)	Cure Temp (b)	Setting (c)	Conc. (d)	Conc. (e)	
I1	-1	-1	-1	-1	-1	
I-2	+1	+1	-1	-1	-1	
I-3	+1	-1	-1	+1	-1	
1-4	-1	+1	- <u>I</u>	+1	-1	
11-1	+L 1	-1 1	- <u>1</u>	-1	+1	
11-2 11-3	-1	· +1	-1	-1 -1	+1 +1	
TT-4	+1	- <u>+</u> +1	<u>1</u>	+1	+1 +1	
IV-1	+1	-1	+1	-1	-1	
IV-2	-1	+1	+1	-1	-1	
IV-3	-1	-1	+1	+1.	-1	
IV-4	+1	+1	+1	+1	-1	
<u>v-1</u>	-1	-1	+1	-1	+1	
V-2 17-3	+1	+1	+1	-1	+1	
V-3 V-4	+⊥ 1	<u>-</u> +1	+1	+1	+1 +1	
• •	±		· •	· T	· 	
III-l	0	0	0	0	0 `	
III-2	0	0	0	0	0	
III-3	0	0	0	0	0	
111-4	0	U	0	U	0	
	Treatme	ent Transforms		Func	tion	
	_	•				
			+1			
Sulfur(a)	1 30%	35%	40%	a=8S	<u>-35</u> 5	
Cure Temperatu (b)	re ^{280°} F	297 ⁰ F	310 ⁰ F	b <u>2(</u> 1n	<u>lnf - ln297)</u> 310-ln 280	
Mill Sett (c)	ing (Th	ree Settings or	n Pump Speed)			
% Vinsol	(ā) ² 1.0	1.3	1.6	d= <u>% v</u>	0.3	
% Redicot AP (e)	e ³ 0.0	0.1	0.2	e=_*	(AP) - 0.1 0.1	
1) \$ of a	aulfur in SEA	<u>.</u>				

TABLE VII Experimental Design, SS Type 2⁵, 1/2 Replicate Factorial Design

.

.

% of sulfur in SEA
 Based on Total Emulsion
 Based upon SEA = 100%

.

Experiment	Data			Effects			
	% Solids	Brookfield Viscosity 100h, 77 F	Code	& Solids	Signi- ficance	Viscosity	Signi- ficance
I-1 I-2 I-3 II-4 II-1 II-2 II-3 II-4 IV-1 IV-2 IV-3 IV-4 V-1 V-2 V-3 V-4 V-3 V-4	54.0 58.7 60.7 56.0 61.3 62.1 62.1 62.0 58.6 58.2 67.5 66.0 67.8 66.0 66.0	31.5 38.9 35.0 27.5 27.5 32.5 33.0 34.5 47.3 53.0 63.0 47.8 83.5 45.3 65.7 55.9	mean a b c d e ab ac bc ad bd cd ae be ce de	61.84 1.35 0.61* 2.11 0.66* 2.43 0.39* 0.21* 0.60* 0.39* -0.05* 0* -1.16* -0.38* 0.25* -0.73*	> 90% > 95% > 99% - - - - - - - - - - - - - - - - - -	44.5 -2.99 -3.82 13.2 0.81* 2.74 1.44* -3.17 -3.37 3.44 -0.06* -0.39* -0.99* -1.37* 2.17* -0.77*	99% >99% ≫99% >95% >95% >99 >99 >99 >99 >99 >99
III-1 III-2 III-3 III-4 mean of III st.dev. of II	63.9 63.5 60.2 61.6 62.3 I 1.72	35.0 36.0 -34.0 34.0 34.75 0.96	replicate replicate replicate replicate mean dev. st. dev.	-1.6* -1.2* 2.1* 0.7* 0.049 0.912		-0.25* -1.25* 0.75* 0.75* 0.07 1.12	
·			t 90 t 95 t 99	1.22 1.60 2.37	t Test.	1.52 2.01 3.04	

TABLE VIII DATA and Effects from experimental Design & Solids and Viscosity

* Used for error determination; replicate deviations, from mean of replicate data.

	Dai	ta			Effects		
Experiment	70h Settlemént mm	Subjective Settlement	Code	70h Settl.	signi- ficance	Sūbj. Assess.	Signi- ficance
I-l	7.6	l (very slight)	mean	3.45	-	3.0	-
I-2	3.5	1	a	0.03*	-	-0.37*	-
I-3	5.4	1	ь	-0.54	> 90%	0.25*	
I-4	3.7	0 (none)	С	-1.18	> 99%	1.75	> 99%
II-l	6.8	1	đ	-0.41*	-	0*	· -
II-2	3.2	3 (slight)	e	-0.61	>90%	-0.13*	-
II-3	3.0	1	ab	-0.17:*	-	-0.37*	-
II-4	3.9	2 (not very slight)	ac	-0.23*	-	-0.37*	-
	3.0	4 (more than slight)	pc	0.53	> 90%	0*	-
IV-2	3.9	8 (very severe)	ad	0.24*	-	0.37*	-
IV-3	3.0	6 (serious)	bđ	0.34*	-	-0.50	> 90%
IV-4	2.4	4	cd	0.23*	-	0.25*	-
V-1	1.6	3	ae	0.52	> 90%	0.25*	-
V- 2	1.3	3	be	0.14*	-	0.13*	-
V-3	1.6	5 (signi- ficant)	ce	-0.19*	-	-0.63	> 95%
V-4	1.4	5	de	0.03*	-	0.37*	-
III-l	3.1	3 rep	licate	0.3*		-0.33*	
III-2	4.3 .	3 rep	licate	-0.9*		-0.33*	
III-3	3.1	4 rep	licate	0.3*		0.66*	
111-4	3.4 (1)	discarded rep	licate	0.3*		-	
Mean of I	II 3.4	3,33					
St. dev.	of 0.6	0.58					
III		mean d	ev.	0.002		0.025	
		st. de (*gro	υφ) υφ)	0.35		0.33	
		······································	t test				
					-		
		+	90	0-47		0.45	
		ť	95	0.62		0.58	
		ť	99	0.94		0.87	
				•			

TABLE IX. DATA AND EFFECTS FROM EXPERIMENTAL DESIGNS

Settlement (Increase in number indicates decrease in quality).

*Used for error determination. Replicate deviations from mean of replicate data.

SEA	
10%	
of	
lons	
ulsi	
Em	
ŝ	
×	
TABLE	

		Notes			1,2	1,2		1,2	1,2	1,2			m	4	ъ		5 gal	sample	•	
		IId	10.4	10.2	10.0	10.6		10.6	10.6	10.6	10.6	11.5	11.0	ı	ı	11.2	11.0			
		Beyond 24 hrs	yes	yes	yes	1		ı	1	ł	yes	I	I	yes	yes	yes	yes			'n.
	tabilit	24 hours	yes	yes	yes	yes		yes	yes	yes	yes	yes	yes	yes	yes	yes	yes			emulsic
	ŝ	off mi11	yes	yes	yes	yes		yes	yes	yes	yes	yes	yes	yes	yes	yes	yes			better
		\$ solids	62	62	ı	1	I	ı	1	ı	ı	53	64	66.5	67.0	67.3	60.0			slightly
*.		Natrosol 250HR	ı	I	1	ı	ı	1-	t	ı	1	ı	0.2	0.09	0.09	0.09	0.065			to make a s
, Nonunal		SPV200 clay	ł	1.0	1	I	1	I	I	I	I	I	I	,. 1	I	1	1			appeared
1, % of Total		Marasperse CE	1	1	ı	ı	0.38	ı	0.38	ı	0.38	0.9	0.7	1	ł	1	0.1			the latter
Formulation		Orzan A	0.38	0.38	0.38	0.38	I	0.38	I	0.38	ı	1	1	ı	ł	ı	ij			trasperse CE,
		Vinsol NVX	1.14	1.14	1.14	1.33	1.33	1.52	1.52	1.71	1.71	2.8	2.0	2.38	2.38	1.98	2.0		Jt.	an A and Ma
		Code	20-16B	20-16Ba	20-32A	20-44A	20-44B	20-44C	20-45A	20-45B	20-45C	20-92A	20-181:29	25-14A	25-15A	25-15B	25-66A	Notes	1. Soft Settlemen	2. Comparing Orza

Best emulsion of the series to that time. Natrosoi aided greatly. Vinsol added to asphalt the night before, sulfur added 2 hours prior to milling. Vinsol added to asphalt the night before, sulfur added at time of milling.

TABLEXI. RS Emulsions of 10% SEA

731 4 25 WTN TX 250HP SolidP So	Fo Dresinate	ormulat PAMAK	ion, % PNMAK	of Tota PAMAK	1, Nominal Dresinate	Natrosol	сю	off	Stabilit	y Beyond		Notes
0.4 $ -$ <t< td=""><td>731</td><td>4</td><td>25</td><td>WCFA</td><td>TX</td><td>250HP</td><td>Solids</td><td>ILIM</td><td>hrs</td><td>24 hrs</td><td>pll</td><td></td></t<>	731	4	25	WCFA	TX	250HP	Solids	ILIM	hrs	24 hrs	pll	
0.8 $ 11.2$ $ 1.0$ $ 11.2$ $ 11.2$ $ 11.2$ $ -$	0.4	1	Ι,	ı	I	ı	ı	yes	оц	ł	11.2	
- 1.0 $ -$ <	0.8	i	ı	ı	I	I	ı	yes	ou	I	11.2	
- $ -$	t	1.0	ı	I	1	i	I	yes	yes	Ю	11.2	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ł	I	1.0	ı	I	I	F	yes	yes	оц	11.0	
- $ -$	I	1	ř.	I	1.0	I I	ı	yes	yes	yes	11.5	
- 1.5 - - - - - yes yes 11.0 1 - - - 0.5 - 0.25 62.8 yes yes yes - 2,3 - - 0.75 - 0.24 59.5 yes yes - 2,3 - - 0.75 - 0.24 59.5 yes yes - 2,3 - - 0.75 - 0.25 62.5 yes yes - 2,3 - - 0.50 - 0.060 65 yes yes - 2,3	1	t	ı	1.0	I	1	ţ.	yes	yes	yes	0.11	
- - 0.5 - 0.25 62.8 yes yes yes - 2,3 - - - 0.75 - 0.24 59.5 yes yes yes - 2,3 - - - 0.75 - 0.24 59.5 yes yes - 2,3 - - - 0.25 62.5 yes yes yes - 2,3 - - 0.50 - 0.060 65 yes yes yes yes 2,5 ga	I	1.5	ł	ı	1	I	ł	yes	yes	yes	0.11	T
- - 0.75 - 0.24 59.5 yes yes yes - 2,3 - - - 0.96 - 0.25 62.5 yes yes yes - 2,3 - - 0.50 - 0.060 65 yes yes yes 2 2,5 ga	I	I	ı	0.5	T	0.25	62.8	yes	yes	yes	ł	2,3
0.96 - 0.25 62.5 yes yes yes - 2,3 0.50 - 0.060 65 yes yes yes - 2,5 ga	I	ı	ı	0.75	1	0.24	59.5	yes	yes	yes	I	2,3
0.50 - 0.060 65 yes yes yes z 2,5 ga	1	I	I	0.96	1	0.25	62.5	yes	yes	yes	ł	2,3
	ı	1	1	0.50	ı	0.060	65	yes	yes	yes	۰.	2,5 ga samle

1. 2.

Soft Settlement Emulsifier added as free acid to asphalt. In addition, 3% PAWAK (based upon sulfur) was added to the sulfur and allowed to cure 2 hours. All emulsions were excellent. Viscosities were excellent.

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		TABLE	XII	Emulsior	is froi	m 10% S	EA Base	e Stoc	ks. CS	ωI						
				Formu	Ilatio	e					I	Sta	abili	ťУ		
Code	Emery 1007	Natrosol 250iR	Indulin W-3	Emery ?	sPV 200 clay	CaC13	Sherex AA57	Armak E-11	Armak E-63	Jetco AE7	с р	mi 11	ъ 4	7 24	NHđ	Ŭ,
							:	İ					i			
20-12N	0.7	ì	1	0.5	۱	0.1	1	I	1	ı	65	yes	ğ	1	2.9	
20-13A	1	ı	1	1	2.0	0.1	1.0	ı	1	1	11	, <u>ខ</u>	1	ı	3+	
20-14A	ı	1	1.0	I	2.0	ı	1	ł	1	I	ł	0u	1	ı	2.3	
20-53D	ł	1	I	I	١	I,	3.0	ł	1	I	I	yes	Qu	I	2.2	
20-58B	ı	1	t	I	۱	1	4.0	1	I	ł		yes	0Ľ	ł	2.2	
20-94A	1	1	5.6	I	١	I	I	ł	ł	I	1	Yes	yes	yes	1.5	7
20-94A/C	1	1	5.6	1	0.5	ł	I	ł	ı	1	ı	Yes	yes	I	1.5	2
20-95A	ı	1	ı	ı	1	1	6.0	ł	ı	1	ı	Yes	yes	yes	2.3	m
20-95B	1	1	ı	1	١	1	I	3.0	ı	1	I	yes	yes	yes	2.2	
20-98A	ł	ł	t	1	۱	1	ı	1	3.0	I	F	yes	yes	ł	1.5	
2098B	ı	1	I	ı	۱	I	ı	ı	ı	3.0	I,	yes	yes	yes	1.5	
20-183:25	ı	0.25	7.0	ı	۱	ı	ł	1	1	ı	50	yes	yes	yes	1.5	4
25-17A	ı	0.065	1.5	ı	۱	ı	I	ı	I	1	64	yes	yes	yes	1.5	5,6
25-17B	ı	0.064	1.5	1	۱	1	ı	ı	1	1	63	yes)	yes	yes	1.5	5,7
25-17C	1	0.065	2.0	t	1	ı	ı	ı	ı	1	54.6	yes]	yes	yes	1.5	5,6
20-10AB	0.7	1	ı	0.5	ı	1	I	1	I	ı	I	yes r	Q	1	3,0	
20-10D	ł	1	1.0	I	1	ł	ı	1	ı	ı	ı	yes r	g	1	2.0	
25-66C	I	0.065	2.0	1	ì	1	ı	I	ı	I	60	yes]	yes	yes	1.8	8
1) Ran emils	tions at	natural of	f of emul	sifiers												
2) Clay adde	xd to 20-	-94A with c	change.	Any chang	le obser	vable w	35									
detriment	al.															
3) Increasir 4) After a n	ng the <i>e</i> r conth thi	mulsifier c is emulsion	content i , was sti	Il stable	tabilit	-Y-										
5) Slight se	ttlement				•											
6) 38 PAMAK	WCFA add	led to sulf	fur, base	d on sulf	ur. 1hr	. cure.										
7) 38 PAMAK	WCFA add	ded to sulf	fur, base	d on sulf	lur. 2h	ır. cure,	, allowed	1 t5 00	olandi	age one	week,	rehea	ated i	c,		
oven to]	20-140%	C before us					1		I							
8) 3% PAMAK	WCFA add	led to sulf	fur, base	d on sulf	ur. 2	hr. cure	e. 5 gall	lon sam	ple.							

.

TABLE XIII.Emulsions from 10% SEA Base Stocks. CQS Stability

			đ¢		24	> 24		
Code	Tyfo A	Tyfo B	Solids	mi11	ᆈ	ᆈ	Hd	Notes
20-55C	1.5	0.5	62	yes	0u	no	2.8	These did not work
20-55D	1.9	0.6	62	yes	ou	QU	3.0	
20-57B	3.0	1.0	62	yes	g	ou	3.6	
20-11C	0.8	0.2	62	2	ı	1	3.0	
		•	•					

TABLEXIV. Emulsions from 10% SEA Base Stocks. CRS

Formulations, % of Totals, Nominal

		tes		г	2	3,4	4	ъ	S		•	2				9		9	7		α	migh			sul	
		ž.																				r FeCl ₃	•	st	to the	
		Ħd	2.3	2.3	3.7	1.6	3.6	3.6	2.0	2.0	3°2	1.2	2.4	2.0	2.0	2.0	2.4	2.5	1.5	2.8	C•7	HCL o		the be	added	
tγ		>24h	ł	I	ł					poor	yes	yes				yes	yes	yes	yes	1	yes	whether	est.	o work	lsion. sulfur.	
ilida:		<u>24h</u>	ou	0	ou	8	8	ğ	g	yes	yes	yes	8	<u>8</u>	01	yes	yes	yes	yes	ou	yes	rmine v	was be	ared to	ed emul	; ;
st		Mill	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes .	yes	yes	yes	Ŷes	to dete	I. IICI	6 appe	improv	
	æ	Solids	70	01.	70	68	68	70	20	70	70	70	60	60	69	69	59	52	48	68	65	iment t	st ació	and AE-	wilder Mak WCF	
	5	1																				5) Exper	be be	5)E 67	7)Vis b 3)3% pn	
	Natros	250HR	1	1	ı	ı	1	1	1	1	I	ł	1	1	1	ł	ı	ı	0.2	ı	0.065			•		
	Jetco	AE6	I	ı	I	ı	1	ı	ı	r	ı	:	ı	1	ı	L	t	0.96	ı	ł	1	•				
	Armak	E67	ı	ł	ı	ł	1	1	1	1	ı	ł	ı	1	1	0.8	ı	1	1.5	1	1. 5	imenta]				
•	Sherex	AA60	1	р I	1	ı	ł	t	1	ł	ł	ı	ı	ı	0.78	ı	۱	ı	ı	ł	I	was detr				
	Sherex	AA-55	1	1	ı	ı	I	ι	1	ı	ı	1	1	انے	1	ı	ı	1	1	ı	1	P. It v			ŋ	
	urmak :	E64	0.	0.	0.	1	:	1	1	1	1	1	ı		1	1	0.	1	1	ı	1	to 20-2		added.	14 hour	
	cex A	<u>5</u>	Г	Т	Г	_		~	~		_	_				,	Т				•	r added	cid	CaCl ₂	: after	
	Sher	-VA	I	1	I	0.4	0. 4	0.6	3 ° 0.	1.6	2.0	2.0	1.5	I	I	1	1	I	I	0.4	1	00 clay	l as a	total)	tlement	
		ode	0-20A	0-20AC	0-21A	0-24B	0-25 N	0-27A	0-27B	0-28A	0-30A	0-30B	0-102A	0-102B	0-103A	0-103B	0-104A	0-104B	0-183:50	0-11B	5-66D	118 SPV 2(Used FeCl	0.1% (on	Soft set	

. .

TABLE XV A

Emulsions of 15% SEA Base Stocks. SS Type

	<u>F01</u>	mulation	1, % of 7	Potal, Nominal	
Code	Vinsol NVX	PAMAK WCFA	Orzan A	Marasperse CE	Natrosol 250HR
20-18A	1.14	-	0.38	-	-
20-33A	1.14	-	0.38	-	-
20-46A	1.33	-	0.38	-	-
20-46B	1.33	-	-	0.38	-
20-46C	1.52	-	0.38	-	-
20-46D	1.52	-	-	0.38	-
20-47A	1.71	-	0.38	-	-
20-47в	1.71	-	-	0.38	-
20-92B	2.28	-	-	0.78	. .
20-159	2.4	-	-	0.8	0.2
20-181:29	1.69	-	-	0.56	.056
25-50L1	2.00	1.7	-	0.60	0.06

			Stabili	ty		
Code	% Solids	<u>Mill</u>	<u>24h</u>	<u>> 24h</u>	_pH	Notes
20-18A	-	yes	-	yes	10.2	soft settlement
20-33A	-	yes	-	-	11.2	good, slight settlement
20-46A	-	yes	-	no	10.5	settlement like 20-46B,
						more than desireable
20-46B	-	yes	-	no	10.1	settlement like 20-46A
20-46C	-	-	problem	with m:	ill inva	lidated test
20-46D	-	-	see 20-	46C		
20-47A	-	yes	yes	no	10.5	1
20– 47B	61.1	yes	yes	no	10.4	1
20-9 2B	63.8	yes	yes	yes	11.5	2
20-159	61.5	yes	yes	yes	10.5	3
20-181:29	71.6	yes	yes	yes	11.0	2
25-50Ll	59.2	yes	yes	yes	11.0	4, 5 gallon

TABLE XV B

Emulsions of 15% SEA Base Stocks. SS Type

- After 5 days, excess sediment, however sediment was soft and readily remixed. Marasperse CE may have slight advantage over Orzan A, however the differences could be within experimental error.
- 2) Emulsion was excellent
- 3) Excellent emulsion, would not mix with slurry sand, however. Very viscous emulsion.
- 4) 3% PAMAK WCFA added to the sulfur (based on sulfur), 2.8% PAMAK WCFA on asphalt. PAMAK and sulfur reacted for at least 2 hours prior to adding to asphalt.

	<u> </u>	'ormula	tion,	s of Total	L, Non	<u>inal</u>	
Code	Dresinate 731	рамак 4	25	Dresinate TX	PAMAK Ins ¹	WCFA In Soap	Natrosol 250HR
20-49A	0.4	-	-		-	-	
20-49B	0.8	-	-	-	-	-	-
20-99A	-	1.0	-	-	-	-	-
20-99B	-	-	1.0	-	-	-	-
20-100A	-	-	-	1.0	-	-	-
20-100B	-	-	-	-	-	1.0	-
20-157	-	2.0	-	-	-	-	0.2
20-158	-	-	-	-	-	2.0	0.2
20-181:60	-	2.0	-	-	-	-	0.2
20-189:1	-	-	-	-	-	2.0	0.2
25-50L20	-	-	-	-	0.3	0.72)	0.7

TABLE XVI A Emulsions of 15% SEA Base Stocks. RS Type

TABLE XVI B Emulsions of 15% SEA Base Stocks. RS Type

		Sta	bility	1		
Code	% Solids	Mill	_24h	>24h	<u>ph</u>	Notes
20-49A	-	yes	no		11.2	Total Loss
-20-49B	-	yes	no		11.2	Total Loss
20-99A	-	yes	yes		11.5	Soft bottom sediment after 24 hr.
20-99B	-	yes	-		11.0	Thick surface layer after 24 hr
20-100A	-	yes	-		-	Same as Above
20-100B	-	yes	-		11.0	Grainy, 85% settled
20-157	62%	yes	yes	yes	11.0	Excellent
20-158	-	yes	yes	yes	10.5	Excellent
20-181:	60 -	yes	yes	yes	11.0	Excellent
20-189:	1 42%	yes	yes	yes	10.8	Excellent
25-50L2	0 65	yes	yes	yes	11.0	5 gallon batch excellent

Reacted with the sulfur for 2 hours at 275^OF.
 Added to asphalt and neutralized in situ during emulsification.

TABLE XVII A

Emulsions of 15% SEA Base Stocks, CSS Type

	\$ Solids	1	1	I	I	I	61.4	61.4	51.2	62	60	64	62	61	61	60	60	60	60
	PAMAK WCFA	I	ł	ı	1	ı	I	1 2	i	I	I	1.8	1.8	0.5	ł	0.27	0.27	0.27	0.27
	Natrosol 250HR		ı	ı	1	ı	0.2	1	0.2	0.2	0.2	0.1	0.1	0.05	0.05	0.1	0.1	0.1	0.1
<u>iominal</u>	Redicote AP	ı	I	ı	1	ı	ı	I	ı	1	1	0.5	0.5	1	ţ	ı	I	ı	ł
Total, n	E-4868	ł	t	ı	i	I	ł	1	1	I	١	1	ı	ł	ı	ı	2	I	2
1, 8 of	1001dN	1	ł	1	1	1	1	1	ı	1	I	1	:	2	1		1	t	1
latior	AE7	ı	ı	ı	1.	٣	ı	ı	Ļ	1	ı	I	ł	ı	1	·1	1	I	1
Formu	Е-63	ı	ı	ı	· m	1	ł	ı	1	ı	1	ł	ı	ı	ı	ı	ı	ı	I
	<u>E-11</u>	I	I	e	ı	ł	: 1	1	, I	1	1	I	ı		ı	1	ı	ı	1
	<u>NA-57</u>	I	2	ì	I	1	ı	ı	I	1	ı	. 1	I	1	ı	I	1	ı	ł
	indulin W-3	2	1	i	ł	1	2.0	2.0	2.0	1.5	2.0	2.7	2.7	ı	2	2	I	2	ı
	Code	20-94B	20-95A	20-95B	20-98A	20-98B	20-160.	20-161	20-183:25	25-18:A	25-18B	25-19A	25-19B	25-37L3	25-37L16	25-46L15	25-461.16	25-47L3	25-471.5

		TI	BLE	XVII	8			
Emulsions	of	15%	SEA	Base	Stoc	ks,	CSS	Type
Form	ilat	ion	. %	of Tot	al,	nom	inal	

<u>Stability</u>

Code	Mill	24h	<u>>24h</u>	pH	Notes
20-94B	yes	no	-	1.5	Grainy, 85% sediment
20-95B	yes	no	-	2.2	Same as above
20-98A	yes	no	-	1.5	Solidified Solidified
20-160	yes	no	-	2.4	Thick layer on surface
20-161 20-183:25	yes ves	no ves	ves	2.2	Complete Loss
25-18:A	yes	no	-	1.5	Failure
25-18B 25-19A	yes yes	no yes	yes	1.5	l, Stable 20 days plus
25-19B	yes	yes	yes	1.5	2, Better than A
25-37L16	<u>-</u>	-	-	4.0	Rough Texture
25-46L15 25-46L16	yes ves	yes ves	yes? no	1.5	4, W-3 better than E4868 4. Reacting PAMAK first
25-4713	yes	yes	no	. -	3, with sulfur produced
25-4/15	yes	yes	no	-	3,/ Detter emulsion

1) Redicote AP, PAMAK WCFA and Sulfur added to asphalt and cured for 2 hours.

2) Redicote AP, 3% PAMAK WCFA (on asphalt) added to asphalt, 3% PAMAK WCFA added to sulfur and cured for 2 hours then sulfur and asphalt blended just prior to emulsification.

3) PAMAK WCFA reacted with sulfur and asphalt.

4) PAMAK WIFA reacted with sulfur first, then added to asphalt.

	CRS Types
A	Stocks,
IIVX	Base
VBLE	SEA
ΞI	15%
	of
	Emulsions

Formulation, % of Total, Actual Solids

\$ Solids	1	1	60.8	59.8	66.0	69.2	66.2	I	ı	47.6	1		
PNMAK WCFA	ſ	,I	ſ	ſ	1	1	1	ı	t	1	0.62		
Natrosol 2501R	I	1	1	I	I	1	ł	0.2	0.2	ı	0.06		
E-67	ł	1	ı	1	ı	0.78	ł	ı	1	1.6	2.0	TIL B	
Varonic T225	1	1	١	i	I	L	1	ı	2.0	ł	1	TABLE XV	
Varonic 0230	ı	1	∣ 1	1	1	1	ł	2.0	ı	1	ì		
E-64	1	I		I	1	ł	0.88	ı	1	ı	¥ 1		
NA-60	· I			1	0.68	ı	ı	I	ı	1	ı		
AA-55	I	'		1.0	1	1	1	1	1	1	ł		
AA-54	- م		C•7		1	1	ı	i	1	1	ı		
Code	20 CCA	ACC-02	4201 0C	201-102	201-1030	20-103B	20-104A	20-148A	20-149	20-183-50	25-47L12		

Emulsions of 15% SEA Base Stocks, CRS Types Formulation, % of Total, Actual Solids Stability

Notes	Thick layer on top	Complete failure	Complete failure	Complete failure	Complete failure	Inverted	, Inverted	Complete failure	Complete failure	After 1 month, non remixable sediment.	Excellent. Perfect after 16 days. Note 1.
Hd	2.0	2.0	2.4	2.0	2.0	2.0	2.0	2.0	3.0	2.0	2.5
 <mark>></mark> 24h	ı	1		ł	1	1	1	I	ı	yes	yes
24h	ou	ou	ou	ou	ou	1	1	ou	ou	yes	Yes
Mill	yes	yes	yes	yes	yes	ou	ou	yes	yes	yes	yes
Code	20-55A	20-58A	20-102A	20-102B	20-103A	20-103B	20-104A	20-148A	20-149	20-183-50	25-47L12

Note #1. 3% PAMNK WEFA (based on sulfur) was reacted with the sulfur for a minimum of 2 hours then added to the asrialt into which 1% PAMAK WEFA had also been added.

	۱ ,		•0	Formulation	n, % of	Total, n	ominal		
	å S in		Orzan	Marasperse	PAMAK	Natrosol		Redicote	dР
Code	SEA	Vinsol	A	· 8	WCFA	250HR	TDA-40	AP	Solids
20-18B	30	3.0	1.0	I	1	I	I	I	I
20-18Ba	30	3.0	1.0	ı	ł	ŀ	ı	ł	ı
20-19A	30	3.0	1.0	ı	1	ı	I	ı	ı
20-19A/C	30	3.0	1.0	1	ł	I	1.0	L	t
20-164A/C	30	2.4	ı	I	I	ı	1.0	.1	ł
Factorial I-1	30	1.0	ı	I	0.49	0.06	I	0	54
I-4	30	1.6	I	1	0.50	0.06	ł	0	56
11-2	30	1.0	1	I	0.55	0.06	ı	0.2	61.5
11-3	30	1.6	1	I	0.56	0.06	I	0.2	62.1
IV-2	30	1.0	I	ł	0.52	0.06	ı	0	58.6
IV-3	30	1.6	1		0.52	0.06	1	0	58.2
1- Λ	8	1.0	ł	ł	0.60	0.06	ı	0.2	66.5
-V-4	30	1.6	ł	ł	0.59	0.06	I	0.2	66.0
I-III	35	1.3	ŀ	1	0.67	0.06	I	0.1	63.9
III-2	35	1.3	1	r	0.67	0,06	t .	0.1	63.5
E-III	35	1.3	ı	ı	0.63	0.06		0.1	60.2
111-4	35	1.3	1	1	0.65	0.06	1	0.1	61.6
I-2	40	1.0	ı	ı	0.70	0.06	1	0	58.7
I-3	40	1.6	I	ſ	0.73	0.06	ı	0	60.7
I-11	40	1.0	1	I	0.74	0.06	ı	0.2	61.3
11-4	40	1.6	1	1	0.74	0.06	ı	0.2	62.0
IV-1	40	1.0	1	ı	0.72	0.06	t	0	60.0
IV-4	40	1.6	I	ı	0.81	0.06	I	0	67.5
V-2	40	1.0	ı	I	0.81	0.06	ı	0.2	67.8
V-3	40	1.6	I	Ì	0.79	0.06	ı	0.2	66.0
20-178A	90 90	1	ł	ı	I	0.06	-	ı	58.3
25-51C10	õ	2.5	F	1	1.34	0.07	ł	I	ı
25-51C22	40	3.0	1	ı	1.74	0.08	ı	ı	ı
25-51C24	40	3.0	1	ı	1.74	0.08	1	ı	ι
25-51C26	40	3.0	1	1	0.74	0.08	1	ı	ı
25-52-A	40	2.88	1	0.8	0.72	0.07	1	I	65.2

TABLE XIX A. Emulsions of 30 and 40% SEA Base Stocks. Slow Set

	St	ability	·		
Code	Mill	24h	>24h	pH	Notes
20-18V	ves	yes	-	10.0	Soft sediment in 14 days
20-18Ba	ves	no	-	10.0	Clay added. complete loss
20-19A	yes	yes	-	10.7	Soft sediment
20-19A/C	yes	no		10.7	Clay added, complete loss
20-164A/C	ves	-	-	11.8	1 / 1
Factorial I-1	ves	ves	ves	-	PAMAK WCFA cured in sulfur
I-4	ves	ves	ves	-	and asphalt blend for 2
II-2	ves	ves	ves	-	hours before making emulsions
II-3	ves	ves	ves	-	See Tables VII and VIII
IV-2	ves	ves	ves	-	for results.
IV-3	ves	ves	ves	-	
V-1	ves	ves	ves	-	TT 11
V-4	ves	ves	ves	-	19 19
TTT-1	ves	ves	Ves	-	
TTT-2	ves	Ves	Ves	-	n tt
TTT-3	Ves	ves	ves	_ ,	H, TF
III-4	ves	ves	ves	- ′	10 10
I-2	ves	ves	ves	-	n (1
I3	ves	ves	ves	-	11 11
II-1	ves	ves	ves	-	11 TI
II-4	ves	ves	ves	-	11 TI
IV-1	ves	ves	ves	-	18 TF
IV-4	ves	ves	ves	-	n H
V-2	ves	ves	ves	· —	PT 17
V-3	ves	ves	ves	-	IF IF
20-178A	ves	no	-	-	Solidified
25-51C10	yes	yes	yes	-	Note #1,
25-51C22	ves.	ves	ves	-	Note #2, settled
25-51C24	yes	yes	vės	-	Note #2, good
25-51C26	ves	ves	no	-	Note #3, unstable
25-52-A	yes	yes	yes	- '	Note #4,

TABLE XIX B.

Emulsions of 30 and 40% SEA Base Stocks. Slow Set

Note 1. 3% PAMAK WCFA cured 2 hours min. with sulfur (based on sulfur), 2% PAMAK WCFA in asphalt. 5 gallon sample. Note 2. 3% PAMAK WCFA cured 2 hours min. with sulfur (based on sulfur), 4% PAMAK WCFA in asphalt. C22 had 0.1% (T) NaOH while C24 had 0.2% NaOH. Marked improvement at the higher caustic soda level. Note 3. No PAMAK in asphalt. Unstable Note 4. 3% PAMAK in sulfur. 5 gallon sample. Soft remixable sediment after 21 days.

XX	
ABLE	
H	ł

Rapid Set	Stability
Stocks.	
Base	
SEA	ыl
408	nomin
and	tal,
30	ę
μ	of
	دين
Emulsions	Formulation,

	\$ sulfur in	PNMAK WCFA	PNMNK WCFA	Natrosol	Tergitol					
Code	SEA	in sulfur	in asphalt	250IIR	15-5-9	Solids	mi11	<u>24h</u>	> 24h	pli Notes
20-163	30	2.00	I	0.20		65.7	yes	8	1	11.8
20-166	30	2.00	1	0.10	0.05	I	yes	20	ı	10.5
20-167	30	2.00		I	I	ł	yes	0u	ı	10.0
20-189-2	30	0.6	1.4	1	I	40	yes	yes	yes	11.0 1) Excellent Emulsion
20-190-1	30	0.6	1.4	0.20	ı	45.1	yes	yes	yes	10.6 1) Excellent
25-47L15	30	0.54	1.5	0.075	i	ı	yes	yes	yes	 2) Excellent
20-190-3	40	0.8	1.2	0.20	I	45	yes	yes	yes	10.4 1)3) Excellent
20-190-2	40	0.8	1.2	0.20	I	53	yes	yes	yes	10.6 1) Excellent
25-51-C20	40	0.74	2.4	0.06	ı	ı	yes	yes	yes	- 2) Excellent

1) PAMAK cured in sulfur one hour, in asphalt 25 minutes. Emulsifier formed in situ when base stock blend of sulfur and asphalt are milled with an aqueous caustic soda solution. Formulations based upon 50% SEA.

2) Formulation based on 60% SEA. PAWAK WYFA cured 2 hours in sulfur before adding sulfur to blend of asphalt and remaining PAWAK WCFA. 5 gallon sample.

3) Sulfur and PAMAK were cured overnight. PAMAK and sulfur appeared as one, similar to Sulphlex.

		Form	nulation	n % on	Total	, Nomi	nal Exc	cept as No	ted	
	% sulfur in SEA	Indulin W-3	AA-57	E-11	E-63	AE-7	Pamak WCFA	Redicote AP	Natrosol 250HR	% Solids
20.010										
20-940	30	2.0	~~~~~	-	-		-	-	-	-
20-95A	30	- .	6.00	-	-	-	_	-		-
20 - 95B	30	. –	-	3.0	-	-	-	-	-	-
20-98A	30	-	-	-	3.0	-	-	-	-	-
20-98B	30	- 11		-	-	3.0	- 1)	- 11	- 1)	-
25-21-(-)	30	2.241	-		-	-	1.361/	0.68*'	0.048*'	68
а	40	2.20	-	-		-	1.40	0.70	0.045	70
b	30	2.24	-	-	-	-	0.68	0.34	0.048	68
ab	40	2.31	-	-	-	-	0.67	0.34	0.050	67
с	30	3.68	-	-	-		1.30	0.33	0.053	65
ac	40	3.57	-	-	-	-	1.32	0.33	0.051	66
bc=e	30	3.36	, -	-	-	_	0.68	0.68	0.048	68
abc	40	3.15		-	-	-	0.70	0.70	0.045	70
d	30	3.39	-	-	-		0.43	0.43	0.171	43
ađ	40	2.24		-	-	-	0.67	0.67	0.099	67
bd=f	30	2.24	-		-		1.34	0.34	0.099	67
abđ	40	2.45	-	-	-	-	1.30	0.33	0.105	65
cđ	30	6.83	-	-	-	-	0.35	0.18	0.195	35
acd	40	5.36	-	-		-	0.49	0.25	0.153	49
bcd	30	3.68	-	-	-	-	1.30	0.65	0.105	65
abod	40	3.78	-	-	_	-	1.28	0.65	0.108	64
25-5A	40	2.01	-	-	-	-	-	0.51	0.19	51.4

TABLE XXI A. Emulsions of 30 and 40% SEA Base Stocks. Cationic Slow Set

1)Actual formulation (not nominal) in factorial. The Redicote AP and the PAMAK WCFA were added to the asphalt and cured for 2 hours. The sulfur was then added and cured 15 or 120 minutes as determined in the design. Cure time was variable b and was 15 minutes where b is absent in the code and 120 minutes where b is present.

	Stab	<u>ility </u>			
Code	mill	_24h	<u>>24h</u>	H	Notes
20-94C	yes	no	-	1.5	Complete Loss
20-95A	yes	no	-	2.3	Solidified
20-95B	yes	no	-	2.2	Grainy, 85% settled
20-98A	yes	no	-	1.5	Solidified
20-98B	yes	no	-	1.5	Solidified
25-21-(-)	yes	no	-		Stirring caused break
a	yes	no	-		Broke
b	yes	no	-		Broke
ab	yes	no	-		Rapid Distress
С	yes	no	-		Rapid Distress
ac	yes	no	-		Rapid Distress
bc=e	yes	no	-		Slow break
abc	yes	no	-		Better than e
đ	yes	yes	no		Appeared like cottage
					cheese, could be mixed
					with H20.
ad	yes	no			Broke
bd=1	yes	yes	no		Paste, nowever accling
					water would make emulsion.
abd	yes	no	-		Distress after awhile,
					better than ab, c or ac.
ca	yes	no			
acd	yes	no			Not marfeet but mod
	yes	yes	yes		NOT PERIECT, DUT GOOD
	yes	no	-		
43-5A	yes	no	-		railed in about 30 Min.

TABLE XXI B Emulsions of 30 and 40% SEA Base Stocks. Cationic Slow Set

TABLE XXII A. Emulsions of Sulphlex

									040	Solids	53.2	52.8	34.0	1	27	43.2	ŀ	41	32.9	38.5		
									Redicote	E-67	l	I	ı	ı	1	1	ı	2.0_{E_1}	2.0'	I		
	ii _				ę				Redicote	AP	1	ı	ı	ł	ł	1	1.0	1.0	I	!		cellent.
	Indul W-3	I	I	I	1.9	I	1		ulin	ñ		1	1	ı	1	1	•	I	1	1		be ex
	dnery 3 752	ı	1	1	1	2.0	1		Ind	M L							2		5.5			ied to
[A A A	1	,	0.	1	,			đ	1001	1	I	I	I	I	2.0	I	I	0.5	0.5		appear
linal.		•	•	2		•	•		PAMAK	WCFA	1.0	1	1.0	1.0	ł	2.0	1	1	:	1		tion a
al, Non	Natroso 250HR	1	ı	0.1	ı	I	1		trosol	OHR	0.2	0.2	0.2	0.2	0.2	0.2	ł	0.25	0.27	0.27		Ir. Reac
f Tot	Drzan A	I	2.0	I	0.9	ı	2.5		n, Na	LJ 25												ne hou
0 %	ote						ر		Vario	CAS	0.5	1.0	I	I	2.0	I	I	I	1	I	1	ted o
tion,	Redic		o.	•	'	'	ö		dulin	W-2		ı	ł	1	1	1	ı	ı	ני ו	4.0'		nd read
rmula	tonite Y	2.5	4.0	ł	2.0	1	1	ŗ	DA In	0	0.	•	1	1	1			1		1		hlex a
0 4	Den Gla								H	4	F	Г										sulp
	Type of of Emulsion	clay	clay	ß	clay-CSS	clay	clay				SI	SS	SI	RS	SS	MS?	CSS	CRS	CRS	CSS		. Added to
	Type of Sulphlex	CDC soft				CDC soft	CDC soft	CDC soft	#61.5 hard	CDC soft	#61.5 hard	CDC soft	CDC soft	CDC soft	CDC soft	l fobetaine	n Sulphlex.					
	·	20-125A	20-1258	20-130	20-134B	20-134A	20-135				20-178B	20-178C	20-188-1	20-188-2	20-188-3	20-188-4	25-2A	25-2B	25–3A	25-3B	1) Coco Su	5) Based c

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Emulsi	
В.	
IIXX	
TABLE	

еx

	S	tability			
Code	<u>mi11</u>	24h	>24h	pli	Notes
20-125A	yes	yes	yes	2	Excessive shot & broke in a few days.
20-125B	yes	yes	yes	3.5	Excellent
20-130	ou	ou	ou	11.2	Emulsion didn't make. Waring Blender
20-134B	no	ou	ou	11	Failed
20-134A	ou	no	ou	11	Made in Waring Blender. Excessive Foam
					No Emulsion
20-135	yes	yes	yes	4	Good
20-178B	yes	yes	no	;	
20-178C	yes	yes	yes	I	Lasted 4 days.
20-188-1	yes	yes	yes	10.5	Excellent 2)
20-188-2	no	ou	ou	ı	Did not make.
20-188-3	yes	yes	ou	9.8	3)
20-188-4	Yes	Yes	yes	10.5	Excellent. 2)
25-2A	yes	yes	yes	2.1	Good. 4)
25-2B	yes	yes	yes	3.2	Good. 4)
25-3A	Yes	ou	I	ı	
25-3B	yes	ou	I		

2) PAMAK WCFA and Sulphlex reacted for 1 hour minimum.

3) Varion CAS (coco sulfobetaine) added to Sulphlex prior to making emulsion.

4) Redicote AP added to Sulphlex. Gas was evolved.
APPENDIX A.

Below is a tabluation of the emulsifiers and other ingredients used in this study. The inclusion of brand names or manufacturer's names is solely for information purposes and is not to imply an endorsement. Emulsifiers differ sufficiently, even if they are of a similar nature, thus it is important for future duplication of this work to detail the materials used.

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Ingredient	Manufacturer	Туре
Vinsol NVX and Resin	Hercules 1 Maritime Plaza Golden Gateway Center Suite 1250 San Francisco, CA. 94111 415-986-2535	Abdiatic acid. Anionic SS emulsifier
Orzan A	Crown Zellerbach Camas, Washington 206-834-4444	Sodium ligno sulfonate. dispersant for SS type emulsions.
Marasperse CE	American Can Company 908 Town & Country Blvd. Suite 230, Houston, Texas 77024	Sodium ligno sulfonate. dispersant for SS type emulsions.
SPV 200 Clay	American Colloid Company 5100 Suffield Court Skokie, Illinois	Bentonite clay
Natrosol 250HR	Hercules	Hydroxyethyl cellulose viscosity builder.
Dresinate 731	Hercules	Anionic PS emulsifier. Rosin Soap
PAMAK 4	Hercules	Anionic RS emulsifier, tall oil.
PAMAK 25	Hercules	Anionic RS emulsifier, tall oil.
Pamak wifa	Hercules	Anionic RS emulsifier, tall oil.
Dresinate TX	Hercules	Anionic RS emulsifier, Rosin Soap.
NP 1007	Emery Industries 8733 S. Dice Rd. Santa Fe Springs, CA. 90670 213-723-8386	nonionic, CSS emulsifier, 100 mole ethoxylated nonyl phenol, 70%
Indulin W-3	Westvaco P.O. Box 5207 North Charleston, S.C. 29406 803-554-8350	Cationic, CSS emulsifier modified ligno sulfonate.
TDA-4 0	Enery	Nonionic, CSS emulsifier, 40 mole ethoxylated tri- decylalcohol.
Arosurf AA-57	Sherex Chemical Company P.O. Box 646 Dublin, Chio 43017	Cationic, CSS emulsifier, amine

Ingredient	Manufacturer	Туре
Redicote E-11	Armak 8401 W. 47th St. McCook, Illionis 60525 313-242-2750	Cationic, CSS emulsifier amine
Redicote E-63	Armak	Cationic, CSS emulsifier, amine
Jetco AE-7	Jetco Chemicals Company P.O. Box 1278	Cationic, CSS emulsifier quaternary amine
Tyfo A	Nacco 14439 South Avalon Gardena, CA. 90248 213-515-1700	Cationic, CQS-CSS emulsifier, amine
Tyfo B	Nacco	Cationic, CQS-CSS emulsifier, lignin derivitive
Arosurf AA-54	Sherex	Cationic, CRS amine
Arosurf AA-55	Sherex	Cationic, CRS amine
Arosurf AA-60	Sherex	Cationic, CRS amine
Redicote E-67	Armak	Cationic, CRS amine with viscosity builder
Jetco AE 6	Jetco	Cationic, CRS amine
Redicote E-4868	Armak .	Cationic, CSS amine
Redicote AP	Armak	Internal dispersant for asphalt, amine
Varonic Q 230	Sherex	Bmilsifier, ethoxylated coco amine
Varonic T 225	Sherex	Emulsifier, ethoxylated tallow amine
Redicote E-64	Armak	Cationic, CRS amine
Tergitol 15-5-9	Union Carbide Corporation 270 Park Avenue New York, N.Y. 10017 212-695-5054	Emulsifier/dispersant ethoxylated nonyl phenol
Varion CAS	Sherex	Emilsifier, coco sulfobetaine
G-752	Sherex	Emulsifier,ethoxylated amine

A-2

APPENDIX A - Supplement 1 Formulation of RS Sulphlex Emulsion

Preparation of Sulphlex Emulsion

A Sulphlex emulsion, based upon the RS type emulsifier, PAMAK WCFA was prepared. 2% PAMAK WCFA (based upon Sulphlex) was added to the Sulphlex and reacted for a minimum of two hours at 275°F. An additional 1% PAMAK WCFA (based upon Sulphlex) was then neutralized with sodium hydroxide to form the soap solution. Sufficient caustic was used to also neutralize the PAMAK WCFA in the Sulphlex. The resulting emulsion appeared to be of excellent quality. The solids were 48%.

APPENDIX A - Supplement 2

Additional Formulation Experiments With Cationic SEA Emulsions

Anionic Emulsions from 10% SEA Base Stocks

5 gallon samples of an RS and SS emulsions were made with the SEA base stock containing 10% sulfur. The emulsions were excellent when produced and when received by ETL. The data on these emulsions are shown in Table I.

The change in formulation which made these emulsions work where previous ones had failed, is that the sulfur was reacted with PAMAK WCFA before being added to the asphalt.

CRS and CSS Emulsions

One quart samples of CRS and CSS emulsions were prepared using the 10% and 15% SEA base stocks. The formulation details are shown in Table I. The CSS emulsions were excellent and appeared to be quite stable over a prolonged period of time. The CRS emulsions appeared to be excellent when first prepared, however upon standing, a thick layer formed along the inside surface of the plastic jars. Based upon these results, five gallon samples of CSS emulsions based on 10% and 15% SEA base stocks were prepared. The 15% sample appeared to be excellent when made, however the 10% sample didn't make. The emulsion from the 15% SEA base stock had some lumps in it the next day. It was remilled to be smooth and shipped to ETL. The sample when received by ETL had a 1° layer of broken emulsion on the bottom. The CSS emulsion of the 10% SEA base stock was prepared after the emulsion made with the 15% SEA base stock. The asphalt used in the 10% SEA base stock was composed of some asphalt from the day before into which had been added Redicote AP and PAMAK WCFA and fresh asphalt to which these materials were added. Apparently day old asphalt into which has been added the Redicote AP and PAMAK WCFA are not readily emulsifiable.

We found that cationic emulsions in quart containers were of superior quality to those in 5 gallon containers. Possibly the sulfur can continue to react and degrade the emulsion in 5 gallon samples, but cool fast enough in the 5 gallon containers to reduce the detrimental effect.

If this is true, considerable difficulty will be experienced in manufacturing these cationic emulsions connercially, especially the CFS type. CRS emulsions are applied hot, thus an emulsion that is not stable at $140-170^{\circ}$ F would be of considerable trouble. While some emulsion plants have heat exchangers, most don't, thus even if the product could be used cold, most producers couldn't cool it.

Cationic Emulsions from 10 and 15% SEA Base Stocks

We were successful in preparing emulsions of 10 and 15% SEA base stocks in one quart samples. The formulation data are shown in Table I. We were not able to make 5 gallon samples, however. It appeared that the length of time that the sulfur and asphalt were with contact with each other prior to emulsification, and the time the emulsions remained hot after emulsification were significant. In the experiment shown in Table I, each of the emulsions was split into two samples, one set of which was cooled immediately, while the other sample was heated at 140 F for 16 hours. As may be seen, the heating was detrimental to the emulsions.

Five gallon samples of the most successful CSS emulsion formulations based upon both the 10% and 15% SEA base stocks were attempted and the samples cooled with cooling coils as fast as possible. The emulsion failed. The data may be seen in Table II. It appears that the length of time that the asphalt and sulfur are mixed together hot affects the quality of the emulsions.

One gallon samples of CSS and CRS emulsions of both the 10 and 15% SEA base stocks were prepared a quart at a time, and those emulsions, which appeared quite good, were sent to Engineers Testing Laboratories for evaluation.

Cationic Emulsions from 30 and 40% SEA Base Stocks

As may be seen in Table II, we were not able to make cationic emulsions from the 30 and 40% SEA base stocks. This does not imply that it is impossible, however we could not find the combination of ingredients that would produce satisfactory emulsions as there were not sufficient funds left in this project to carry out more research.

Effect of Temperature on Emulsion Quality

Sulfur will react with asphalt and the emulsifiers. In fact, one of the ingredients, PAMAK WCFA (a tall oil) is added specifically to the sulfur to react with it prior to making emulsions. Previous work has shown that the PAMAK WCFA must be added to the sulfur and reacted for at least two hours prior to blending the sulfur with the asphalt. If the asphalt is added with the PAMAK WCFA, the emulsions are poor. Our recent studies now indicate that the length of time the emulsion is stored hot can influence quality, and also the length of time the asphalt and sulfur are mixed together prior to emulsification. This is especially a factor with the cationic emulsions. The anionic emulsions were produced without much difficulty.

To make large quantities of cationic emulsions which contain sulfur, the sulfur and asphalt phases should be introduced into a static mixer just prior to emulsifying and the emulsion should be passed through a cooler prior to going into storage.

Sulfur Extended	Temperature.
158	orage
J	3
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Formulatic	. Effect
lsion	Stocks
Ha Ha	Base
Η,	비
TABLE	Aspha

					CSS Bm	lsifiers				CRS Emulsif	ier	
Formulation, Nominal	н	Ia	д	del	Ħ	IIa	Ħ	IIab	H	IIIa	f	IIIab
Asphalt Husky AC20	51.0	. 51.0	51.0	21.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0
Sulfur	9.0	0.6	9.0	0.6	0°6	0.6	9.0	9.0	9.0	0.6	0.6	9.0
PAMAK WCFA	0.18	0.36	0.18	0.36	0.18	0.36	0.18	0.36	0.18	0.36	0.18	0.36
Armak Redicote AP	0.26	0.26	0.51	0.51	0.26	0.26	0.51	0.51	0.26	0.26	0.51	0.51
W-3 Indulin	4.2	4.2	4.2	4.2	ı	ı	ı	1	F	I		ı
AA57	ı	ı	ı	ł	2.0	2.0	2.0	2.0	ı	ı	1	ł
AA54	ı	1	ı	ı	ı	I	I	I	2.0	2.0	2.0	2.0
Natrosol 250 HR	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
HCI 35% conc.	i	ı	I,	,	•	1	•		0.8	0.8	0.8	8.0
Properties												
Solids	65	65	66	65	62	61	64	63	64	64	64	59
Stability, Room Temp.	fail	ð	poor	¥	fail	poor	fair	satisfactory	fail	satisfactory	boot	poop
140 ⁰ F	failed	failed	failed	failed	failed	failed	failed	failed	fail	poor	poor	poor
Opments 1) Susi rap.	tained to idly cool	Imperature (of 140 ⁰ F f	or 16 hr ca	use an ac	xelerated.	degradat	ion of emulsi	on qual	lity compared	with nat	urally or
2) Emu	lsion qu	ality improv	ved as the	i level of s	surface ac	tive compo	unds incr	eased to the	limits	of the experi	iment.	

TABLE II. Nominal Emulsion Formulations of from 10 to 40% Sulfur Extended Asphalt Base Stock

	40	SEA	30	SEA	15 SEA	10 SEA	15.9	SEA	10	SEA
	CRS	CSS	CRS 20 760	CSS	CSS	CSS 20 27	CSS	CRS	CSS	CRS
	407-67	707-67	007_C7	107-27	17-67	23-2/B	N67-67	767-67	967-67	1167-67
Asphalt, Husky AC20	36,0	36	42.0	42.0	51.0	54.0	51.0	21. 0	54.0	54.0
Sulfur	24	24	18	18	0.6	6.0	9.0	0.6	6.0	6.0
INMAK WOFA	0.96	0.96	0.72	0.72	0.36	0.24	0.36	0.36	0.24	0.24
Armak Redicote AP	0.36	0.36	0.42	0.42	0.51	0.54	0.51	0.51	0.54	0.54
Romah TAE-DR (75)	ı	2.0	1	2.0	ı	ı	ı	ı	ı	ı
Sherex AA57	1	ı	1	1	2.0	2.0	2.0	ı	2.0	ı
Sherex AA54	2.0	ı	2.0	1	ı	I	ı	2.0	 1	2.0
Hercules, Natrosol	250HR 0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Acid, HCl 35% conc.	0.8	0.007	0.8	0.007	0.007	0.007	0.001	8.0 .	0.001	0.8
Batch Size	l at	1 gt	1 gt	1 gt	5 gal	5 gal	4 x 1gt	4 x lqt	4 x lq	: 4 × 1qt
Properties										
Measured & Solids	55	55	52	23	60	57	54	57	56	61
Stability	failed	failed	failed	failed	failed	failed	good	good	good	good
Comments	For impr 1) The emuls 2) Mechanica 3) PAMAK and should no	coved resu sions shou al action I Redicote ot be made	lts the fa ld be cool upon the a must be a until jus	actors below led as soon smulsions es added to the st prior to	v should be n as possible specially whe sulfur and emulsificati	oted: after millir n hot accele asphalt respon.	g. rates brea ectively h	king. Wt the b	lend of	the two

APPENDIX B MODIFIED DISTILLATION PROCEDURE

INTRODUCTION

The standard ASTM D244-80 emulsion distillation test was not used with the modified sulfur-water emulsions formulated during this project due to the requirement of heating the emulsion to 500F (260C) during the test which could result in evolution of H_2S and SO_2 and possibly a considerable change in residue characteristics. Therefore, a modified distillation procedure consisting of heating the emulsion to 260F (127C) and sweeping with CO_2 was developed.

Apparatus

100 ml boiling flask

Condenser tube

Connecting apparatus consisting of rubber stopper to fit flask, delivery tube, and stopper to fit the condenser

Thermometer - ASTM 113C

Aeration tube - 9 inch (22.9 cm) long, 1/8 inch (0.3 cm) diameter glass tubing

Electric heating mantle controlled by a variable rheostat

Heating mantle support consisting of ring stand and appropriate clamps

CO₂ source and adequate flow regulators

Gas flowmeter

Graduated cylinder, 100 ml capacity

 CO_2 heating apparatus consisting of a beaker, oil, copper coil, and a hot plate.

Procedure

- Assemble apparatus. A schematic of the assembled apparatus is shown in Figure Bl0.
- Thoroughly stir emulsion and add 250 grams to the previously weighed boiling flask (weight including thermometer, stoppers, aeration tube, and delivery tube), place the flask into the heating mantle, and connect to the condenser.

- 3. Begin heating the emulsion with the electric heating mantle.
- 4. Begin introducing warmed CO_2 (oil bath at 135C) at a rate of 1 to 2 liters/minute when the temperature of the emulsion reaches 200F (93C) with the bottom of the aeration tube approximately 1/2 inch above the top level of the emulsion.
- 5. Adjust the transformer so that the emulsion boils as rapidly as possible without boiling over.
- 6. When emulsion temperature reaches 260F (127C), lower aeration tube into the emulsion (bottom of tube approximately 1 cm from the bottom of the flask) and continue CO introduction.
- 7. Maintain the 260F (127C) temperature for 30 minutes to complete the distillation.
- 8. Remove flask, with thermometer and delivery apparatus, allow to cool and weigh.
- 9. Calculate percent residue as:

 $\frac{F - I}{E} \times 100\%$ in which:

- F = final weight of flask delivery apparatus, and residue
- F = initial weight of flask and delivery apparatus
- E = initial weight of emulsion
- 10. To remove residue from the boiling flask, heat the flask and residue to 260F (127C) in an oven and pour residue into an 8 ounce tin.



Schematic Diagram of Modified Distillation Apparatus

FIGURE 10

APPENDIX C PHYSICAL PROPERTIES OF EMULSIONS

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CR S1 5	RSSX
DA	40.8	34.9	39.9	34.6	38.0	34.3	37.8	29.4	33.1	-	-	-	-	45.4
T A	39.9	35.1	41.2	35.8	37.9	33.7	37.9	30.0	32.5	-	-	-	2	48.9
X	40.3	35.0	40.5	35.2	37.9	34.0	37.8	29.7	32.8	-	1	- '	-	47.1
s	0.8	0.2	1.2	1.1	0.1	0.5	0.1	0.5	0.5	-	-	-	- '	3.1
C۷	2.0	0.6	3.0	3.1	0.3	1.5	0.3	1.7	1.5	-	-	-	-	6.6

 $q_{crit} = 0.694$ q = 0.513

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 13 One-Way ANOVA Summary, Water Content by Distillation

Source	df	ss	MS	F	F.05	<u>F.01</u>
Mixture	9	431.2	47.91	55.3	3.02	4.94
Error	10	8.7	.87			
Total	19	439.9				



Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE	11	Newman-Keuls Ranking, Water Content h	by
		Distillation	-

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D A T A	37.1 40.5	35.1 34.6	41.0 41.2	36.5 36.4	39.7 38.0	34.1 33.5	38.0 39.9	30.2 30.1	32.4 33.8	42.0 43.3	38.5 38.3	42.1 42.3	37.6 38.4	40.9 39.6
X S Cv	38.8 3.0 7.7	34.8 0.4 1.1	41.1 0.2 0.5	36.4 0.1 0.3	38.8 1.5 3.9	33.8 0.5 1.5	38.9 1.7 4.4	30.1 0.1 0.3	33.1 1.2 3.6	42.6 1.2 2.8	38.4 0.2 0.5	42.2 0.2 0.5	38.0 0.7 1.8	40.2 1. 2 3.0

$$q_{crit} = 0.522$$

$$q = 0.266$$

TABLE 15 One-Way ANOVA Summary, Water Content by Evaporation

Source	df	SS	MS	F	<u>F.05</u>	<u>F.01</u>
Mixture	13	343.9	26.5	28.80	2.43	3.87
Error	14	12.9	0.92			
Total	27	956.8				-

CSS10 CSS15 SS10 RSSX SS30 SS15 SS10 CRS10 CRS15 RS10 RS10 RS15 RS40 RS30

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 12 Newman-Keuls Ranking, Water Content by Evaporation

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
DA	-0.1	-	0.7	0.1	0.6	-0.2	0.0	-1.1	30.7	-	-	_	+	59.6
TA	1.3	-	0.3	0.5	-0.1	0.5	0.4	-0.3	35.8	-	-	1	-	60.4
x	0.6	-	0.5	0.3	0.25	0,15	0.20	-0.7	33.3	1	-	-	-	60.0
s	1.2	-	0.4	0.4	0.62	0.62	0.4	0.7	4.5	-	-	-	-	0.7-
C٧	207	-	70.9	118	248	413	177	101	13.6	-	-	-	-	1.2

$$q_{crit} = .750$$
 $q = .722$

TABLE 17 One-Way ANOVA Summary, Storage Stability

Source	df	SS	MS	F	<u>F.05</u>	<u>F.01</u>
Mixture	8	7427.2	928.4	544.2	3.23	5.47
Error Total	<u>9</u> 17	15.3 7442.5	1.7			

ss10^{*} RSSX RS40 SS10 RS10 SS15 SS30 RS15 RS30

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

> FIGURE 13 Newman-Keuls Ranking, Storage Stability .

TABLE 18 Fr

Freeze Thaw Resistance

		Re	plication	1 1	Re	plication	1 2
Emul	sion	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
SS	10*	H**	н	H	Н	н	Н
RS	10*	В	В	B	В	В	В
SS	10	H	Ħ	Н	н	H	H
RS	10	В	В	В	В	В	В
SS	15	В	В	В	В	в	В
RS	15	н,Т	В	в	H,T	В	В
SS	30	В	В	В	В	В	В
RS	30	H	H,T	Н,Т	н	H	H,T
CSS	10	В	В	В	В	в	В
CRS	10	В	В	В	в	В	В
CSS	15	В	В	В	·B	В	В
CRS	15	В	В	В	В	В	В
RS	SX	В	В	В	В	В	В

Notes: * = PAMAK WCFA not reacted with sulfur

- **H = homogeneous
 - B = broken
 - T = thickened

as judged by stirring with a glass stirring rod and visual examination

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
DA	15.0	0.5	18.5	4.0	11.0	5.5	11.5	5.5	5.0	40.0	. 24.0	30.0	30.0	20.0
T A	16.5	0.5	18.5	4.2	13.0	6.0	10.8	6.7	6.0	38.5	22.0	30.0	31.0	20.0
x	15.8	0.5	18.5	4.1	12.0	5.8	11.2	6.1	5.5	39.3	23.0	30.0	30.5	20.0
S	1.3	0.0	0.0	0.2	1.8	0.4	0.6	1.1	0.9	1.3	1.8	0.0	0.9	0.0
C۷	8.4	0.0	0.0	4.3	14.8	7.7	5.6	17.4	16.1	3.4	7.7	0.0	2.9	0.0

 $q_{crit} = 0.522$ q = 0.169

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 20 One-Way ANOVA Summary, Emulsion Break Time

Source	df	SS	MS	F	F.05	<u>F.01</u>
Mixture	13	3505.1	269.6	451.5	2.43	3.87
Error	14	8.4	0.60			
Total	27	3513.5				

CSS10 CRS15 CSS15 CRS10 RSSX SS10 SS10 SS15 SS30 RS30 RS15 RS40 RS10 RS10

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 14 Newman-Keuls Ranking, Emulsion Break Time

TABLE 21 Saybolt Furol Viscosity, 77F; sec

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CS\$10	CRS10	CSS15	CRS15	RSSX
D	239	45.2	71.7	45.0	45.8	74.9	65.6	121	20.2	25.9	31.7	28.0	25.8	18.8
Ť	213	44.0	72.7	44.0	45.0	66.4	67.5	140	20.1	27.3	31.5	28.2	26.3	19.3
x	226	44.6	72.2	44.5	45.4	70.7	66.6	13.1	20.2	26.6	31.6	28.1	26.1	19.1
s	23.0	1.1	0.9	0.7	7.5	1.7	16.8	0.1	1.2	0.2	0.2	0.4	0.4	0.4
Cv	10.2	2.4	1.2	2.0	1.6	10.7	2.5	12.9	0.4	4.7	0.6	0.6	1.7	2.3

$$q = .473$$

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 22

One-Way ANOVA Summary, Saybolt Fural Viscosity

Source	df	SS	MS	<u>F</u>	F.05	<u>F.01</u>
Mixture	13	81738.1	6287.5	157.26	2.43	3.87
Error	14	559.8	39.98			
Total	27	82297.8				

SS10* RS30 SS10 RS15 SS30 SS15 RS10 RS10* CRS10 CSS15 CSS10 CRS15 RS40 RSSX

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 15 Newman-Keuls Ranking, Saybolt Fural Viscosity TABLE 23

Coating Ability of Sulfur Water Emulsions $^{f 1}$

			Dry	Aggregate	Wet	Aggregate
Designa	on ation	Replication	Coating	After Rinse	Coating	After Rinse
SS 10)*	1	G ²	P	G	G ³
		2	G	P	G	P
SS 10)	1 2	G G	P P	Ġ G	P P
RS 10)	1 2	G F	P P	· P P	P P
SS 15	5	1 2	G G	P P	G G	P P
RS 15	5	1 2	G G	G G	P^4_P4	р ³ Р
SS 30)	1 2	G G	P P	G G	P P
RS 30	C	1 2	GG	F F	G G	F F
RS 40	0	1 2	G G	P P	. G G	P P
CSS 10	0	1 2	G G	P P	G G	P P
CRS 10	0	1 2	G G	F F	G G	G G
CSS 1	5	1 2	G G	P P	G G	F P
CRS 1	5	1 2	G G	면 도	G G	G G
RS S	х	1	G	P	G G	P P

NOTES:

* PAMAK WCFA not reacted with sulfur

1. The RS 10* emulsion broke prior to testing

2. G = Good Coating, F = Fair Coating, P = Poor Coating

3. Emulsion foamed during mixing

4. Emulsion appeared to break during mixing and would not coat.

]	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	26.8	-	32.2	42.7	47.1	10.6	32.4	10.5	35.7	50.4	37.0	52.3	46.4	10,0
TA	28.2	-	37.9	47.4	39.5	9.4	45.9	12.5	37.6	50.9	35.3	51.3	46.3	9.1
x	27.5	1	35.1	45.1	43.3	10.0	39.2	11.5	36.7	50.7	36.2	51.8	46.4	9.6
s	1.2	-	5.1	4.2	6.7	1.1	12.0	1.8	1.7	0.4	1.5	0.9	0.1	0.8
Cv.	4.5	-	14.4	9.2	15.6	10.6	30.6	15.4	4.6	0.9	4.2	1.7	0.2	8.3

$$q_{crit} = 0.560$$
 $q = 0.395$

TABLE 25 One-Way ANOVA Summary, Water Miscibility

Source	df	SS	MS	F	<u>F.05</u>	<u>F.01</u>
Mixture	12	5433.4	452.8	37.91	2.63	4.00
Error	13	155.3	11.9			
Total	25	5588.7				



Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 16 Newman-Keuls Ranking, Water Miscibility

TABLE 26 Residue Content by Distillation; %

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	59.2	65.1	60.1	65.4	62.0	65.7	62.2	70.6	66.9	-	-	-	-	54.6
Ť	60.1	64.9	58.8	64.2	62.1	66.3	62.1	70.0	67.5	-	-	-	-	51.1
х	59.7	65.0	59.5	64.8	62.1	66.0	62.2	70.3	67.2	1	-	1	-	52.9
s	0.8	0.2	1.2	1.1	0.1	0.5	0.1	0.5	0.5	-	-	-	-	3.1
C٧	1.3	0.3	1.9	1.6	0.1	0.8	0.1	0.8	0.8	-	-	-	-	5.9

$$q_{crit} = 0.694$$
 $q = 0.513$

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 27 One-Way ANOVA Summary, Residue Content by Distillation

Source	df	SS	MS	<u>F</u>	<u>F.05</u>	F.01
Mixture	9	431.2	47.91	55.30	3.02	4.94
Error	10	8.7	.87			
Total	19	439.9				

RS30 RS40 RS15 RS10 RS10 SS30 SS15 SS10 SS10 RSSX

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 17 Newman-Keuls Ranking, Residue Content by Distillation

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 1 5	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	62.9	64.9	59.0	63.5	60.3	65.9	62.0	69.8	67.6	58.0	61.5	51.9	62.4	59.1
Ť	59.5	65.4	58.8	63.6	62.0	66.5	60.1	69.9	66.2	56.7	61.7	57.7	61.6	60.4
х	61.2	65.2	58.9	63.6	61.2	66.2	61.1	69.9	66.9	57.4	61.6	57.8	62.0	59.8
s	3.0	0.4	0.2	0.1	1.5	0.5	1.7	0.1	1.2	1.2	0.2	0.2	0.7	1.2.
C٧	4.9	0.7	0.3	0.1	2.5	0.8	2.8	0.1	1.9	2.0	0.3	0.3	1.1	1.9

 $q_{crit} = 0.522$ q = 0.266

*Note: PAMAK WCFA not reaced with sulfur.

TABLE 29One-Way ANOVA Summary, Residue Content by
Evaporation

Source	df	SS	MS	F	F.05	<u>F.01</u>
Mixture	13	343.9	26.5	28.80	2.43	3.87
Error	14	12.9	0.92			
Total	27	356.8				

RS30 RS40 RS15 RS10^{*} RS10 CRS15 CRS10 SS10^{*} SS15 SS30 RSSX SS10 _CS515 CSS10

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 18 Newman-Keuls Ranking, Residue Content by Evaporation

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
DA	0.8	-	0.0	71.6	10.3	70.2	0.7	33.5	32.5	0.5	0.2	0.3	0.2	30 .3
Ă	0.2	-	0.0	80.2	10.8	68.0	0.8	35.7	24.7	0.4	0.2	0.3	0.2	32.1
x	0.5	-	0.0	75.9	10.6	69.1	0.8	34.6	28.6	0.5	0.2	0.3	0.2	31.2
s	0.5	-	0.0	7.6	0.4	1.9	0.1	1.9	6.9	0.1	0.0	0.0	0.0	1.6
Cv	106	-	0.0	10.0	4.2	2.8	11.8	5.6	24.2	19.7	0.0	0.0	0.0	5.1

 $q_{crit} = .560$ q = .422

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 31 One-Way ANOVA Summary, Demulsibility; %

Source	df	SS	MS	F	F.05	<u>F.01</u>
Mixture	12	17476.3	1456.4	255.24	2.62	4.00
Error	13	74.2	5.71			
Total	25	17550.5				

RS10 RS15 RS30 RSSX RS40 SS15 SS30 SS10* CSS10 CSS15 CRS15 CRS10 SS10

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 19 Newman-Keuls Ranking, Demulsibility

121

TABLE 32

LONG TERM STABILITY OF SEA AND SULPHLEX EMULSIONS

Emu	lsion	Time⊥ (<u>Months</u>)	Notes
SS	10*	12	Contained small broken globules which could not be suspended
RS	10*	12	Broken, solid residue
SS	10	3	Good
RS	10	3	Good, slight settlement, easily suspended
SS	15	12	Thick settlement, but could be restirred
RS	15	12	Thick settlement, but could be restirred
SS	30	12	Broken, semi-solid residue
RS	30	12	Thick settlement, but could be restirred, small broken globules
RS	40	12	Broken, semi-solid residue
CSS	10	1.5	Good
CRS	10	1.5	Good, no settlement or separation
CSS	15	1.5	Beginning to break, slight water separa- tion and small asphalt globules present
CRS	15	1.5	Good, slight settlement
RS	Sulphl	.ex 7	Slight settlement and separation of water and residue, slight of trying to break

Note: 1 Age at examination from date of production

APPENDIX D PHYSICAL PROPERTIES OF EMULSION RESIDUES BY DISTILLATION AND EVAPORATION

TABLE 33 Penetration of Residue From Distillation, 77F, 100g; 1/10 mm

·	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
DA	128	88	62	111	75	120	111	-	67	1	-	-	1	9
T A	99	83	88	114	70	105	90	-	62	-	-	-	-	6
x	114	86	75	113	73	113	101	-	65	-	-	-	-	8
s	25.7	4.4	23.0	2.7	4.4	13.3	18.6	-	4.4	-	-	-	-	2.7
C٧	22.6	5.2	30.7	2.4	6.1	11.8	18.5	-	6.9	-	-	-	-	35.4

TABLE 34 One-Way ANOVA Summary, Penetration of Distillation Residue

Source	<u>df</u>	SS	MS	F	<u>F.05</u>	<u>F.01</u>
Mixture	8	18398.0	2299.8	18.19	3.23	5.47
Error	_9	1138.0	126.4			
Total	17	19536.0				

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 20 Newman-Keuls Ranking, Penetration of Distillation Residue

TABLE	35	Absolute	Viscosity	of	Residue	From
		Distil	lation, 1	40F	Poise	

	no IU	5510	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
729	919	1601	816	977	867	-		-	-		-	-	
390	1183	1711	799	940	824	-	-	-	-	-	-	-	-
310	1051	1656	808	959	846	-	-	-		-	-	-	-
143	234	97	15	33	38	-	-	-	-	-	-	-	
7.6	22.3	5.9	1.9	3.4	4.5	-	-	-	-	-	~	-	
7 3 	29 90 10 43 7.6	29 919 90 1183 10 1051 43 234 7.6 22.3	29 919 1601 90 1183 1711 10 1051 1656 43 234 97 7.6 22.3 5.9	29 919 1601 816 90 1183 1711 799 10 1051 1656 808 43 234 97 15 7.6 22.3 5.9 1.9	29 919 1601 816 977 90 1183 1711 799 940 10 1051 1656 808 959 43 234 97 15 33 7.6 22.3 5.9 1.9 3.4	29 919 1601 816 977 867 90 1183 1711 799 940 824 10 1051 1656 808 959 846 43 234 97 15 33 38 7.6 22.3 5.9 1.9 3.4 4.5	29 919 1601 816 977 867 - 90 1183 1711 799 940 824 - 10 1051 1656 808 959 846 - 43 234 97 15 33 38 - 7.6 22.3 5.9 1.9 3.4 4.5 -	29 919 1601 816 977 867 - - 90 1183 1711 799 940 824 - - 10 1051 1656 808 959 846 - - 43 234 97 15 33 38 - - 7.6 22.3 5.9 1.9 3.4 4.5 - -	29 919 1601 816 977 867 - - - 90 1183 1711 799 940 824 - - - 10 1051 1656 808 959 846 - - - 43 234 97 15 33 38 - - - 7.6 22.3 5.9 1.9 3.4 4.5 - - -	29 919 1601 816 977 867 - - - - 90 1183 1711 799 940 824 - - - - 10 1051 1656 808 959 846 - - - - 43 234 97 15 33 38 - - - 7.6 22.3 5.9 1.9 3.4 4.5 - - -	29 919 1601 816 977 867 - <	29 919 1601 816 977 867 - <	29 919 1601 816 977 867 - <

$$q_{crit} = .949$$
 $q = .460$

TABLE 36 One-Way ANOVA Summary, Absolute Viscosity of Distillation Residue

Source	df	SS	MS	F	F.05	<u>F.01</u>
Mixture	5	1.06-E06	2.12-E05	22.84	4.39	8.75
Error	б	.06-E06	9269			
Total	11	1.11-E06				



Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 21 Newman-Keuls Ranking, Absolute Viscosity of Distillation Residue

TABLE 37 Ductility of Residue From Distillation, 77F, 5 cm/min; cm

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	100	-	64	100	31	37	38	30	23	-	-	-	1	-
Ť	100	-	72	100	34	44	30	43	27	-	-	-	<u>с</u>	-
х	100	-	68	100	33	41	34	37	25	-	-	-	-	-
s	0.0	-	7.1	0.0	2.7	6.2	7.1	11.5	3.5	-	-	-	-	
Cν	0.0	-	10.4	0.0	8.2	15.3	20,8	31.6	14.2	-	-		-	-

$$q_{crit} = .793$$

TABLE 38 One-Way ANOVA Summary, Ductility of Distillation Residue

Source	df	SS	MS	F	F.05	<u>F.01</u>
Mixture	7	13234.4	1890.6	81.54	3.50	6.18
Error	8	185.5	23.2			
Total	15	13419.9				

ss10 [®]	RS10	\$S10	RS15	RS 30	SS30	SS15	RS40

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 22 Newman-Keuls Ranking, Ductility of Distillation Residue

TABLE 39 Penetration of Residue From Evaporation, 77F, 100g; 1/10 mm

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
DA	91	107	87	107	84	70	50	65	61	149	87	113	128	-
Ă	76	128	96	114	66	119	81	69	50	147	108	122	129	-
x	84	118	92	111	75	95	66	67	56	148	98	118	129	-
5	13.3	18.6	7.9	6.2	15.9	43.4	27.5	3.5	9.7	1.8	18.6	8.0	0.9	<u>ت</u> ه
C۷	15.9	15.8	.8.7	5.6	21.3	45.9	41.9	5.3	17.6	1.2	19.0	6.8	0.7	-

 $q_{crit} = .560$ q = 0.274

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 40 One-Way ANOVA Summary, Penetration of Evaporation Residue

Source	<u>df</u>	SS	MS	<u>F</u>	<u>F.05</u>	<u>F.01</u>
Mixture	12	17854	1487.9	7.52	2.63	4.00
Error	13	2573	197.9			
Total	25	20427				

CSS10 CRS15 CSS15 RS10^{*} RS10 CRS10 RS15 SS10 SS10^{*} SS15 RS30 SS30 RS40

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 23 Newman-Keuls Ranking, Penetration of Evaporation Residue

TABLE	41	Absolute	Viscosity	' of	Residue	From
		Evapor	cation, 14	0F;	Poise	

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	1325	640	1636	708	1261	645	-	-	-	1560	1541	1364	1284	-
Ť	1055	762	2111	791	1194	727	-	-	-	1140	1850	1281	1085	-
x	1190	701	1784	750	1228	686	-	+	-	1350	1696	1323	1185	-
S	239	108	420	74	59	73	-	-	-	372	274	74	176	-
Cv	20.1	15.4	22.5	9.8	4.8	10.6	-	-	-	27.6	16.1	5.6	14.9	· _

 $q_{crit} = .694$

$$q = .233$$

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 42 One-Way ANOVA Summary, Absolute Viscosity of Evaporation Residue

Source	<u>df</u>	SS	MS	<u>F</u>	F.05	<u>F.01</u>
Mixture	9	2.91-E06	3.23-E05	9.95	3.02	4.94
Error	10	0.32-E06	.32-E05			
Total	19	3.23-E06				

SS10 CRS10 CSS10 CSS15 SS15 SS10 *CRS15 RS10 RS10 RS15

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 24 Newman-Keuls Ranking, Absolute Viscosity of Evaporation Residue

TABLE 43 Ductility of Residue From Evaporation, 77F, 5 cm/min; cm

	SS 10	RS 10	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RSSX
D	38	-	100	100	47	18	16	35	100	100	100	100	100	- ·
TA	28	-	100	100	46	18	23	39	100	100	100	100	100	-
X	33.0	-	100	100	46.5	18	19.5	37.0	100	100	100	100	100	-
s	8.9	-	0.0	0 .0	0.9	0.0	6.2	3.5	0.0	0.0	0.0	0.0	0.0	-
C۷	26.8	-	0.0	0.0	1.9	0.0	31.8	9.6	0.0	0.0	0.0	0.0	0.0	-

 $q_{crit} = .598$ q = .463

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 44 One-Way ANOVA Summary, Ductility of Evaporation Residue

Source	df	SS	MS	<u>F</u>	F.05	<u>F.01</u>
Mixture	11	29096	2645	382.43	2.72	4.23
Error	12	83	6.92			
Total	23	29179				

SS10 RS10 RS40 CSS10 CRS10 CSS15 CRS15 SS15 RS30 SS10* SS30 RS15

Note: Emulsions which share a common underline are not significantly different at the 0.05 confidence level.

FIGURE 25 Newman-Keuls Ranking, Ductility of Evaporation Residue



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