HIGHWAY BINDER MATERIALS
FROM MODIFIED
SULFUR-WATER EMULSIONS

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FINAL REPORT

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16. Abstract

This project had the objectives of developing and characterizing stable modified-sulfur water emulsions using sulfur-extended-asphalt and Sulphlex as base stocks. Anionic and cationic emulsions which had rapid and slow setting characteristics were studied. Standard asphalt emulsion formulations using base stocks containing sulfur produced unstable emulsions which settled excessively. Reaction of a tall oil with sulfur and asphalt separately, and increased emulsifier concentrations resulted in successful emulsions. Settling characteristics were improved by adding a hydroxyethyl cellulose viscosity builder to the continuous phase. Thirteen sulfur-extended-asphalt emulsions and one Sulphlex emulsion were produced and then characterized using ASTM D244 and several non-standard test procedures. Emulsion properties are compared to ASTM D977 and D2397 requirements.

The study concludes that it is possible to formulate and produce stable modified sulfur-water emulsions using sulfur-extended-asphalt or Sulphlex as base stocks. These emulsions have many characteristics which are comparable to standard asphalt emulsions.

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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-extended-asphalt 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 sulfur-extended-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 sulfur-extended-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-extended-asphalt 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.

TABLE 1

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

	% Sulfur (by weight of Total Mix)				
Property	0	10	15	30	50
Absolute Viscosity, 140F, 30cm Hg; Poise	670.4	384.0	367.1	-*	-*
Penetration, 77F, 100g, 5 sec; 1/10 mm	133	182	216	226	186

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

TABLE 2

FORMULATIONS OF SULPHLEX SAMPLES

Sulplex Designation	Formulation
No. 233	70% Sulfur, 12% CDC, 10% DP, 8% VT
No. 233 CDC	Same as No. 233 except supplied from a smaller batch
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
CT = Coal Tar
DPCD = Dicyclopentadiene

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.

TABLE 3

PENETRATION AND ABSOLUTE VISCOSITY OF UNAGED AND RTFOT AGED SULPHLEX SAMPLES

	Penetration; 77F, (25C) 100g; 1/10 mm		Absolute	Absolute Viscosity, 140F (60C); Poise		
Sulphlex Designation	Unaged	RTFOT[1] Residue	% Retained Penetration	Unaged	RTFOT[1] Residue	Aging[2] Index
No. 233	139	8	6	966.1	54,166.2	56.1
No. 233 CDC	169	74	44	106.0	1,285.4	12.1
No. 233 DCPD	142	30	21	1055.1	13,920.0	13.2
No. 126	13	9	69	–[3]	44,418.0	–[3]
No. 230	82	41	50	2999.0	10,499.0	3.5

Note:

[1] Residue from rolling thin film oven test.

[2] Aging Index = $\frac{\text{RTFOT Residue Viscosity}}{\text{Unaged Viscosity}}$

[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 closer to those of a medium set. Therefore, modified 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.

PHYSIOCHEMICAL TYPE
EMULSION SET TYPE
BINDER TYPE

		SULFUR EXTENDED				SULPHLEX			
		10%	15%	30%	40%	1*	2	3	4
ANIONIC	RS	—	—	—	—	—	—	—	—
	MS	—	—	—	—	—	—	—	—
	SS	—	—	—	—	—	—	—	—
CATIONIC	RS	—	—	—	—	—	—	—	—
	MS	—	—	—	—	—	—	—	—
	SS	—	—	—	—	—	—	—	—

*Note: Signifies four different Sulphlex Formulations

FIGURE 1 Emulsion Formulation Experiment Matrix

TABLE 4

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 cellulose viscosity builder.
Dresinate 731	Hercules	Anionic PS emulsifier. Rosin Soap
PAMAK 4	Hercules	Anionic PS emulsifier, tall oil.
PAMAK 25	Hercules	Anionic RS emulsifier, tall oil.
PAMAK WCFA	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-40	Emery	Nonionic, CSS emulsifier, 40 mole ethoxylated tridecylalcohol.
Arosurf AA-57	Sherex Chemical Company P.O. Box 646 Dublin, Ohio 43017	Cationic, CSS emulsifier, amine

TABLE 4, continued

Ingredient	Manufacturer	Type
Redicote E-11	Armak 8401 W. 47th St. McCook, Illinois 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	Emulsifier, 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	Emulsifier, coco sulfobetaine
G-752	Sherex	Emulsifier,ethoxylated amine

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:

$$Y_{ij} \quad = \quad \mu + E_i + \varepsilon_{ij}$$

in which:

Y_{ij} = response variable
μ = effect of overall mean
E_i = 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.

EMULSION DESIGNATION

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

*Note: PAMAK WCFA not reacted with sulfur.

FIGURE 2 Experimental Analysis Matrix

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.

TABLE 5 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

NOTE:

[1] SS 10* and RS 10* initial formulations without PAMAK WCFA reacted in sulfur

[2] Emulsifier percentages are based on total emulsion weight

[3] PAMAK 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 CO_2. 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 SO_2 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.

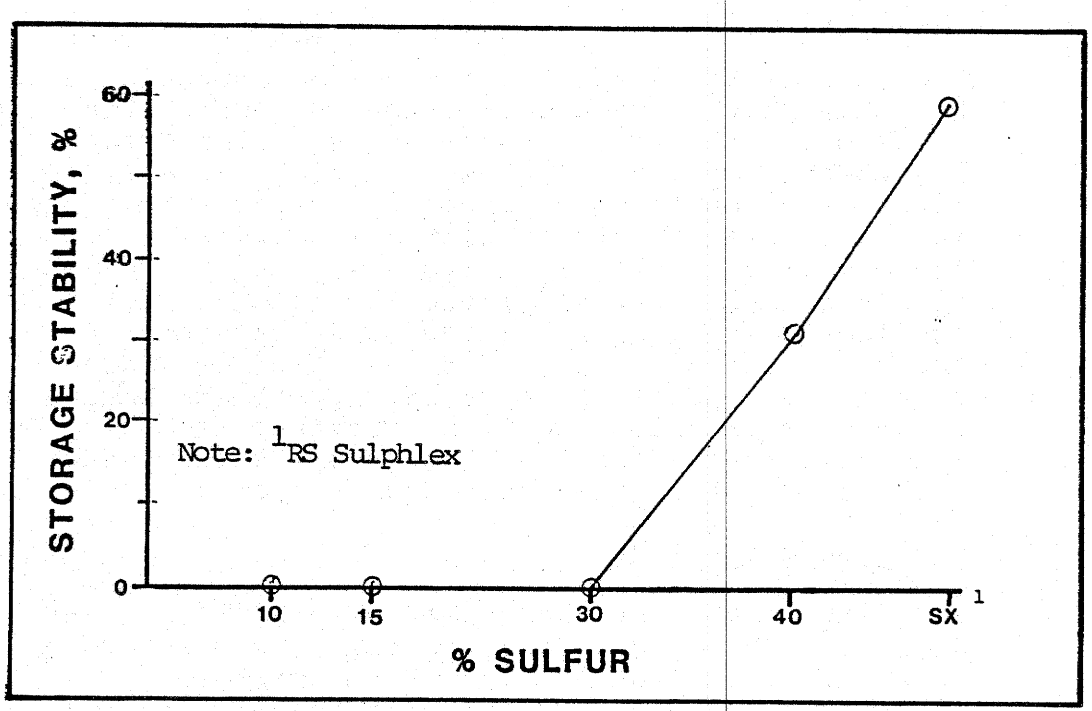

FIGURE 3   Storage Stability versus Percent Sulfur in Binder

TABLE 6

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

Sieve Size	% Passing
3/4 in (19.0 mm)	100
1/2 in (12.5 mm)	75
3/8 in (9.5 mm)	50
1/4 in (6.3 mm)	25
No. 4 (4.75 mm)	0

Bulk Specific Gravity	2.835
Absorption	1.1%

TABLE 7

SPECIFIC GRAVITIES OF EMULSIONS AND RESIDUES

Emulsion	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

<u>Note</u>:

*PAMAK WCFA not reacted with sulfur.

[1] Measured volumetrically using a 250 ml pycometer at 77F

[2] Calculations based on evaporation residue content

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 Coating Ability

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.

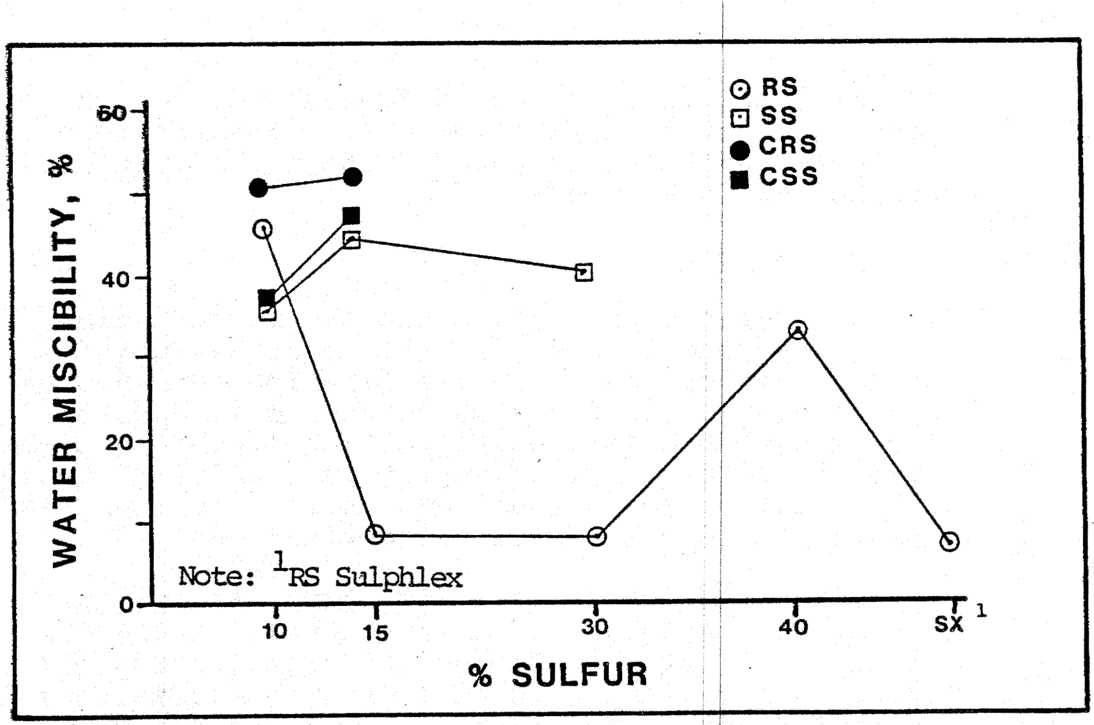

FIGURE 4 Water Miscibility of Sulfur-Water Emulsions

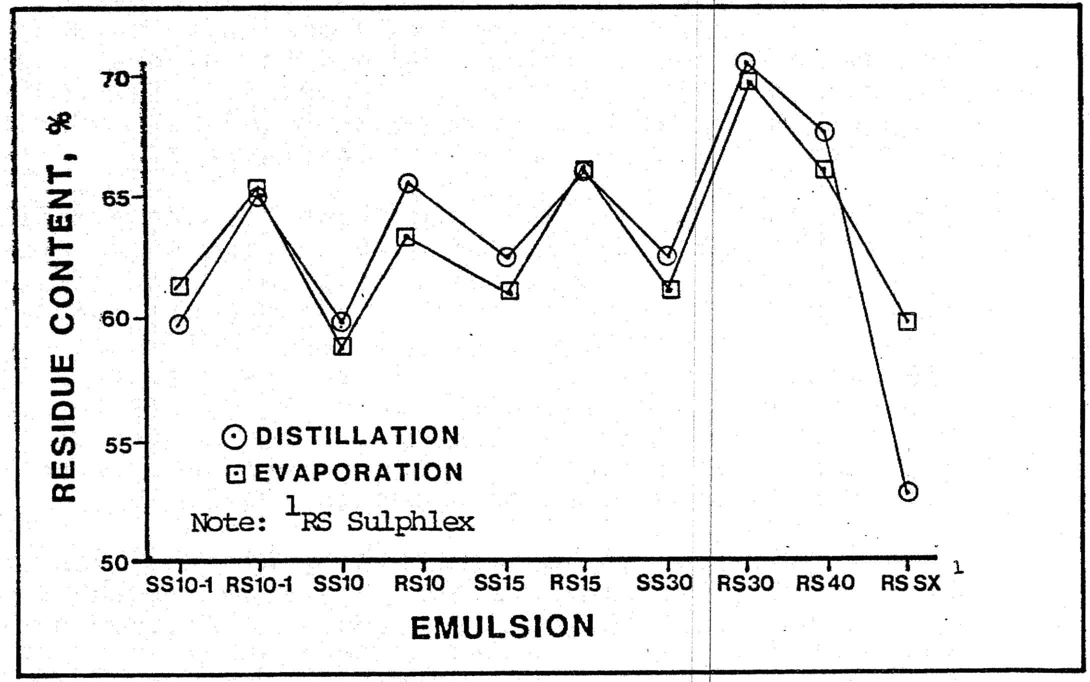

FIGURE 5 Comparison of Residue Contents by Distillation and Evaporation

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 $CaCl_2$ 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 $CaCl_2$ 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.

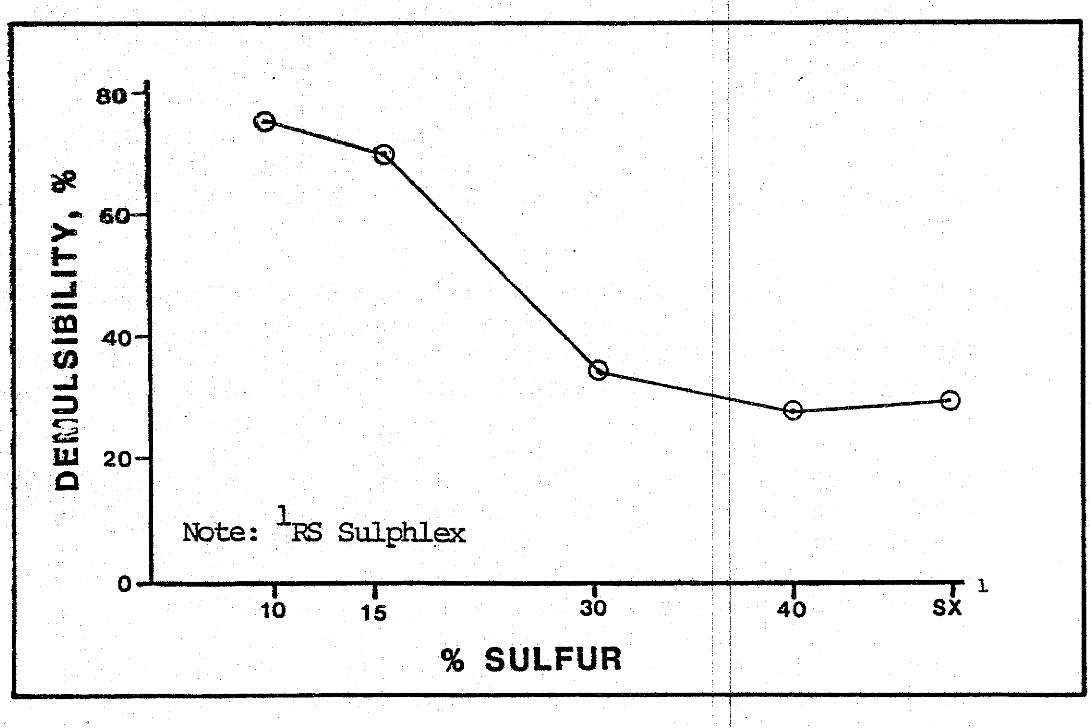

FIGURE 6 Demulsibility of Anionic Rapid Set Emulsions

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 signficant 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).

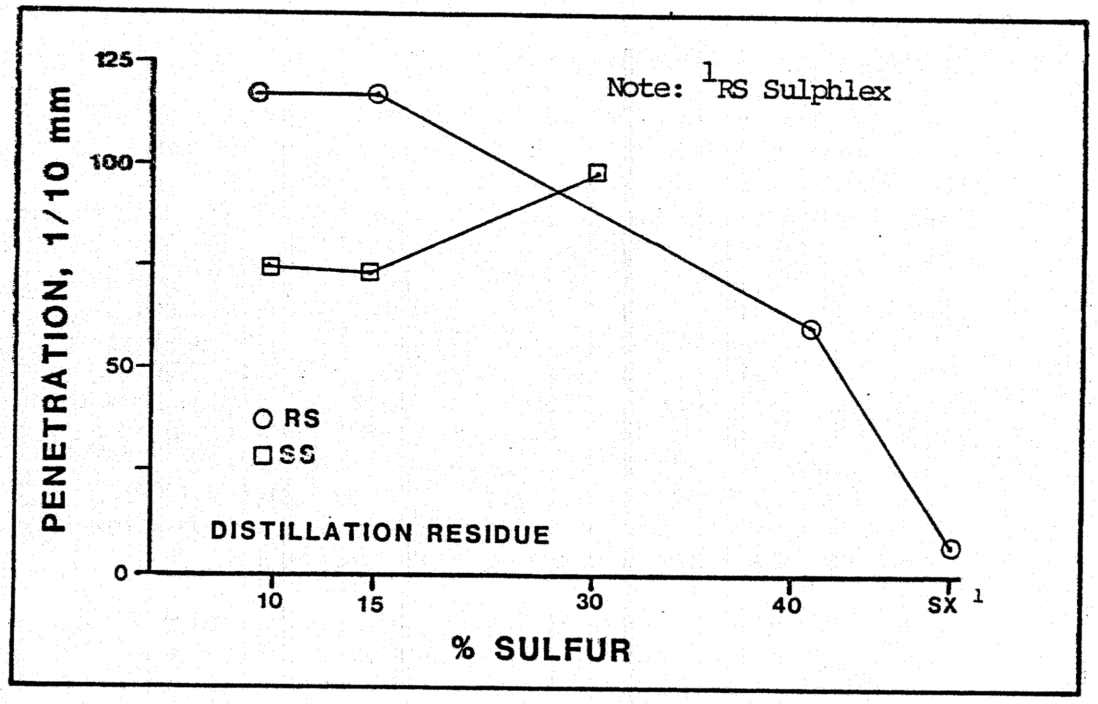

FIGURE 7 Penetration at 77F (25C) of SS and RS Emulsions

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

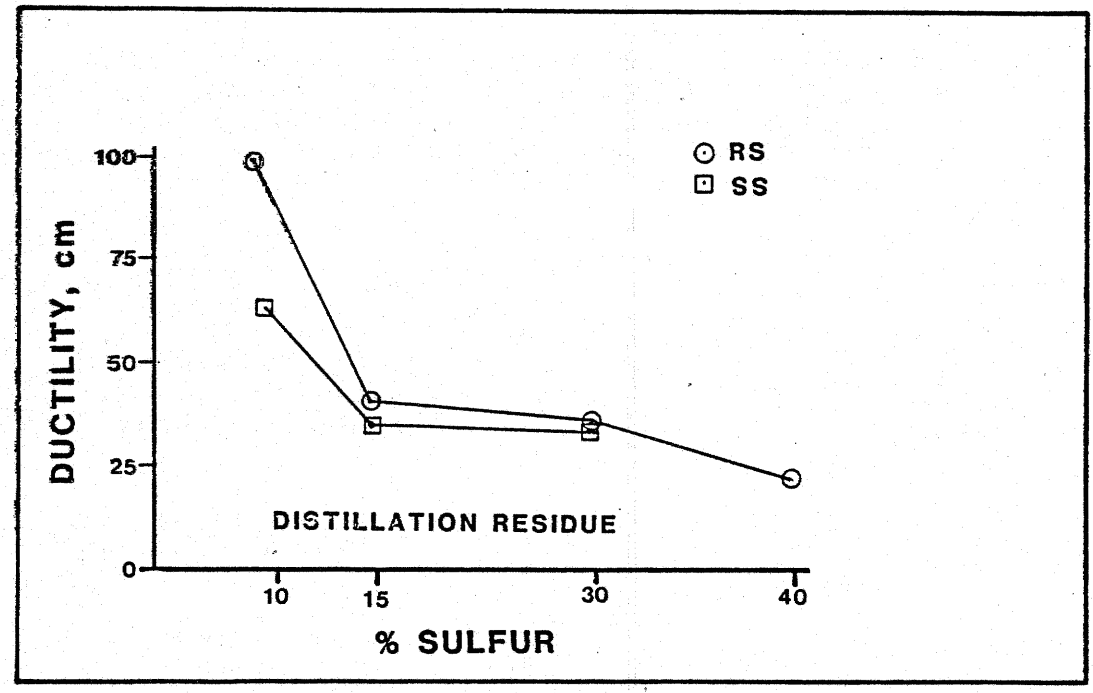

FIGURE 8 Ductility at 77F (25C) of Distillation Residues

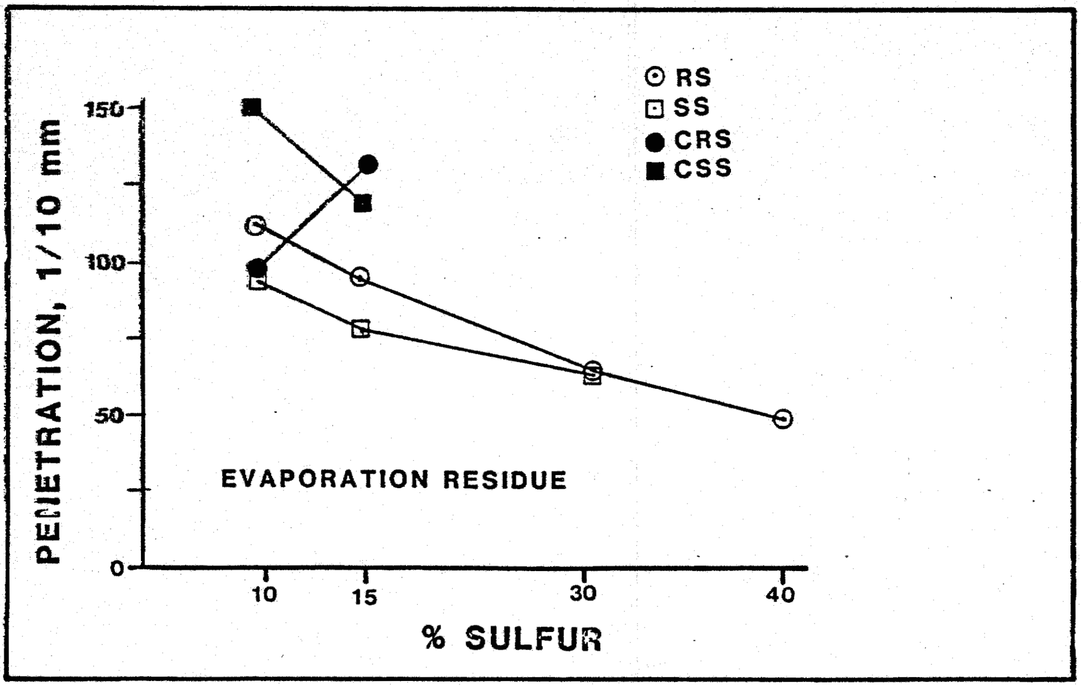

FIGURE 9 Penetration at 77F (25C) of Evaporation Residues

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-1h 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-1h 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-1h 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.

TABLE 8

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

Property	SS 10*	SS 10	SS 15	SS 30	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	1 max
Residue by Distillation; %	59.7	59.5	62.1	62.2	57 min
Tests on Residue:					
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	100+	68	33	34	40 min

Note: [1] Requirement for SS-1h emulsion.

TABLE 9

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

Property	Emulsion Designation						Spec. Limits
	RS 10*	RS 10	RS 15	RS 30	RS 40	RSSX	
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; %	-	0.3	0.15	-0.7	33.3	60.0	1 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

TABLE 10

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

Property	CSS 10	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:

[1] Determined by the evaporation procedure

[2] Specified by the distillation procedure

[3] Determined on evaporation residue

[4] Specified 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.

TABLE 11

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

Property	CRS 10	CRS 15	Specification Limits
Tests on Emulsifier:			
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]	100-250[4]
Ductility, 77F (25C), 5 cm/min; cm	100+[3]	100+[3]	40 min[4]

Notes:

[1] Determined by the evaporation procedure

[2] Specified by the distillation procedure

[3] Determined on evaporation residue

[4] Specified 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. Sulphur-extended-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.

1. 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.

2. Addition of a viscosity builder (Natrosol 250 HR) to modified sulfur-water emulsions reduces settlement.

3. Successful cationic SEA emulsions are more difficult to formulate than successful anionic SEA emulsions.

4. 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.

6. 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.

1. 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.
6. Investigate the properties of SEA and Sulphlex emulsion-aggregate mixtures for various paving uses such as surface, base, and open graded friction courses.
7. 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:

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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.

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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

1. As the percent of added sulfur increases, the difficulty in making emulsions also increases.

2. 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

1. 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.

4. 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°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

Asphalt. 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 ¼ to ½ 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 $P = \{(a, b \ldots n) \mid a \in [-1, +1], b \in [-1, +1] \ldots n \in [-1, +1]$ with the center point = (0,0......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 CO_2 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°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.

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*"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 SO_3 , CN^-, RS^-or HS^- 7)8) . There is also evidence that R_3N: and R_3P: nucleophides will cause chain sission 9-11). Thus the cationic emulsifiers, being amines, may very well catylize the sission of the S-S bond and accelerate the reaction of sulfur with asphalt.

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

The reaction has been suggested to be;

$$A-S-S-B+R_3N \longrightarrow R_3N^{+}+AS^{-}+SB$$

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°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 did not look bad, although reversible agglomeration had occurred. The base stock was Sulphlex.

Use of Unsaturated Fatty Acids

In discussing our problem with Dr. Michael Raymond[13], it appeared that molecules with double bonds might be caused to react with sulfur. If such a material also had a water soluble or potentially water 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 WCFA (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 pitch[2]), 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, ½ 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
X_2= high level
X_1= low level
$\therefore a \in [-1, +1]$

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	C
-	-1	-1	-1
a	+1	-1	-1
b	-1	+1	-1
ab	+1	+1	-1
c	-1	-1	+1
ac	+1	-1	+1
bc	-1	+1	+1
abc	+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 regression 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 1s are eliminated for convenience).

Experiment	Treatment							
	M	A	B	AB	C	AC	BC	ABC
⊖	+	−	−	+	−	+	+	−
a	+	+	−	−	−	−	+	+
b	+	−	+	−	−	+	−	+
ab	+	+	+	+	−	−	−	−
c	+	−	−	+	+	−	−	+
ac	+	+	−	−	+	+	−	−
bc	+	−	+	−	+	−	+	−
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 geometry which will greatly aid in evaluating the experiment. First of all, all columns vectors, X_i of $\mathbf{X}$, the experimental matrix are orthognal, that is, the vector product $X_i^T X_j = 0, i \neq j$ The regression equation is $\mathbf{Y} = \mathbf{X}\beta + \epsilon$ where ϵ = error and $\hat{Y} = X\hat{\beta}$ is the least squares estimator, $\mathbf{Y}$ is the matrix of observed data and $\mathbf{X}$ 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.

$\hat{\beta}$ are the least squares estimator for the experiment. This equation can be rearranged to

$$\hat{\beta} = (X^T X)^{-1} X^T$$

X^T = transpose of X

This particular type of design results in $X^T X = m\,I$ where

$x_i \in X, \quad i = 1, 2 \cdots m,$ $\qquad I$ = Identity matrix

Thus $(X^T X)^{-1} = 1/m\ I$ and

$$\therefore \hat{\beta} = \frac{1}{m} I X^T Y$$

$\hat{\beta}_1$ is the mean while the other $\hat{\beta}_i, i \neq j$ represent the deviation from the mean.

If one finds that many of the $\hat{\beta}_i$ 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,....,0) may be run to obtain an independent estimate of error. The total sum of squares is given by

$$SS_T = y^T y$$

and that from regression;

$$\begin{aligned} SS_{Reg} &= \hat{\beta}^T X^T X \hat{\beta} \\ &= \hat{\beta}^T (m I) \beta \end{aligned}$$

error of course is

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

In our studies, the matrix $\hat{\beta}$ was separated into two matrices; $\hat{\beta}_1$ & β_2 such that $\hat{\beta}_1$ included those which were felt to be significant while those of β_2 were used for error. SS_{Reg} then became

$$ss_{reg} = \hat{\beta}_1^T (m I) \hat{\beta}_1$$

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

<u>CSS Emulsion. 30 and 40% Sulfur in SEA.</u> 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 interaction 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.

SS Emulsion. 30 and 40% Sulfur in SEA. 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)
d.	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.)

$m \equiv -abcde$ $d \equiv -abce$ $bc \equiv -ade$ $ae \equiv -bcd$

$a \equiv -bcde$ $e \equiv -abcd$ $ad \equiv -bce$ $be \equiv -acd$

$b \equiv -acde$ $ab \equiv -cde$ $bd \equiv -ace$ $ce \equiv -abd$

$c \equiv -abde$ $ac \equiv -bde$ $cd \equiv -abe$ $de \equiv -abc$

(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, Brookfield 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.

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* 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 noted 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 PAMAK 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% Indulin 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 $FeCl_3$ as an acid in place of HCl. The thought being that the Fe^{+++} ion could pick up the sulfide and reduce the H_2S odor. No great effect was found, and it appeared that the emulsion in which HCl 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 soap 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 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
PAMAK WCFA	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:

	Sulfur in SEA	
	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.

	% Sulfur in SEA	
	30%	40%
PAMAK WCFA		
in sulfur	0.54	0.74
in asphalt	1.50	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.

<u>Emulsions from 30 and 40% SEA Base Stocks. Cationic Rapid Set.</u> 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.

<u>Emulsions of Sulphlex.</u> 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 <u>XXII</u>. 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.

<u>Improving the Dispersion of Sulfur in the Asphalt.</u> 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 tall oil-sulfur 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.

Clay Emulsions. 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 1. Emulsion Mill #1

Modified Centrifugal Pump as Mill

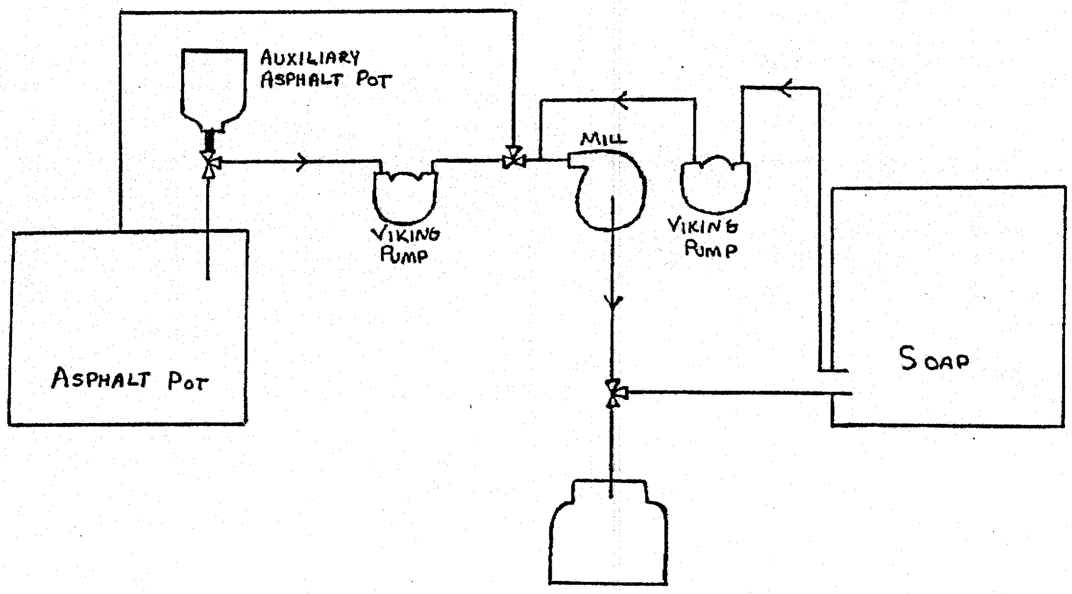

Figure 2. Emulsion Mill #2

Charlotte

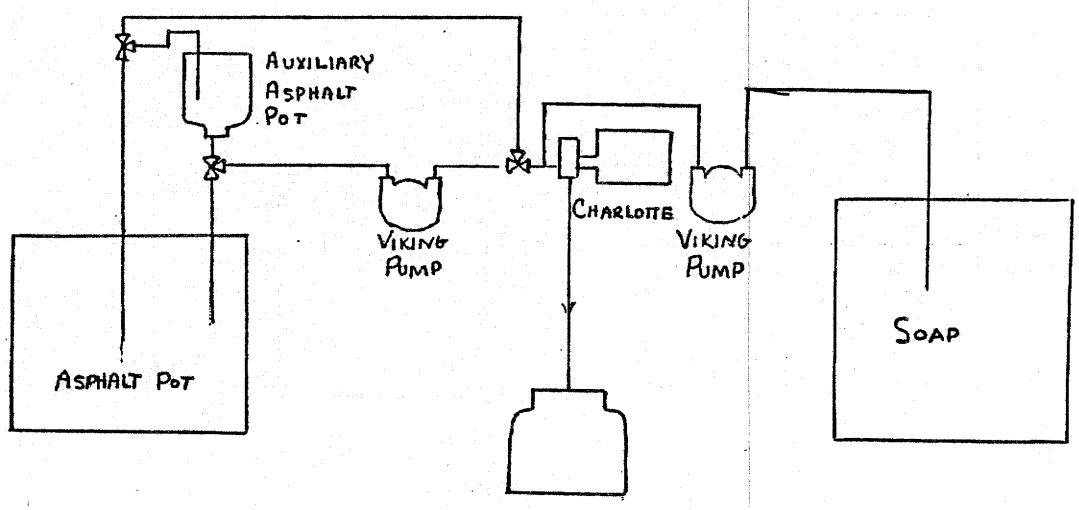

Figure 3

Disposable Viscometer

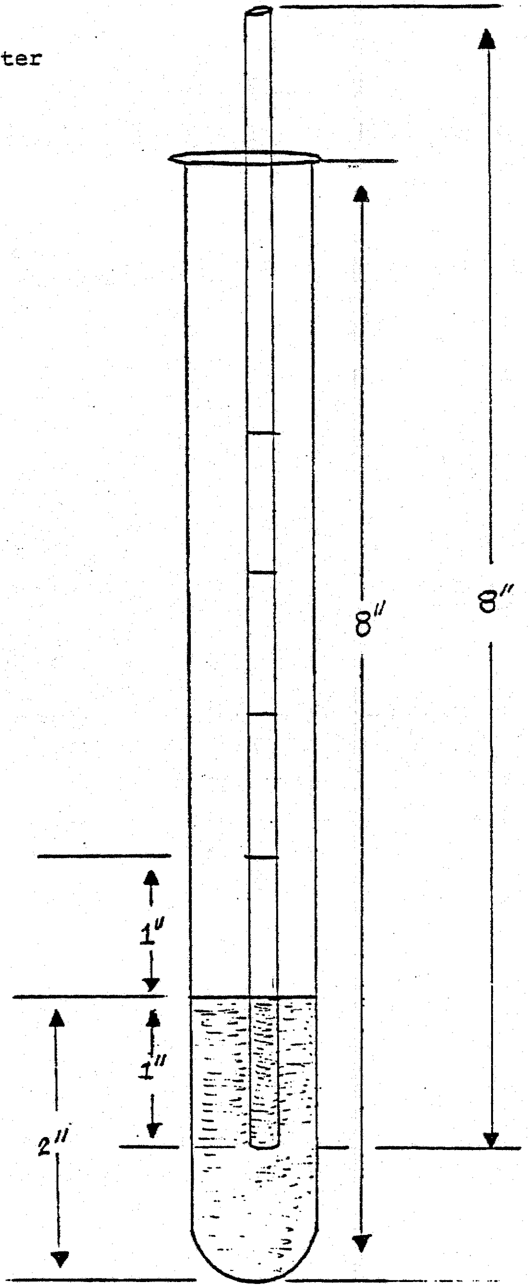

TABLE I.

Effect of Emulsion Distillation on Base Stock Properties

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

TABLE II.

Properties of Asphalt-Sulfur Base Stocks
Asphalt-U.S. Oil Co. AR 2000 Emulsion Base Stock

% Sulfur (weight)	Viscosity @140°F, poises	Penetration @77°F, dmm
0	670.4	133
10	384.8	182
15	367.1	216
30	1)	226
50	1)	186

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

TABLE 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 to run the viscosity.

TABLE IV. EXPERIMENTAL DESIGN, CSS TYPE

2^6, 1/4 Replicate Factorial Design

Experiment	Treatments					
	Sulfur (a)	Reaction Time (b)	Indulin W-3 (c)	% Natrosol (d)	% Redicote AP (e)	% PAMAK final
-	-1	-1	-1	-1	+1	+1
a	+1	-1	-1	-1	+1	+1
b	-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
d	-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

	Treatment Transforms		Function
	-1	+1	
Sulfur (a) 1)	30%	40%	$a = \frac{\%S-35}{5}$
Reaction Time, h (b)	0.25	2.00	$b = \frac{t-1.125}{0.875}$
Indulin W-3 (c) 2)	20%	30%	$c = \frac{(W\text{-}3)-25}{5}$
Natrosol (d) 3)	0.15	0.30	$d = \frac{N-0.225}{0.075}$
Redicote AP (e) 4)	0.5	1.0	$e = \frac{(AP)-0.75}{0.25}$
PAMAK WCFA (f) 4)	1	2	$f = \frac{P-1.5}{0.5}$

1) % of sulfur in SEA
2) % of 35% solution in emulsifier phase
3) in emulsifier solution
4) on dispersed phase

TABLE V.

DATA MATRIX Y

2^6, 1/4 Replicate

Experiment	% Solids	Brookfield Viscosity1)	Order of Quality2)
-	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
d	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 $\hat{\beta}$

2^6, 1/4 Replicate

Experiment	% Solids	Brookfield Viscosity	Quality
mean	62.3	12.9	8.5
a(sulfur)	4.9*	-2.1*	-3.5 > 99%
b(reaction time)	8.0>95%	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>99%	-2.6 >90%	3.25 >99%
ad	3.9*	1.9*	-1.25*
bd=f(PAMAK WCFA)	7.9>95%	-4.9 >99%	1.25*
abd	-4.9*	-0.38*	0.25*
cd	-3.1*	1.9*	-1.25*
acd	-1.4*	-1.6*	-0.25*
bcd	13.9>99%	2.6 >90%	2.75 >95%
abcd	0.9*	1.1*	-2.75 >95%
Mean deviation 1)	0.29	0.38	-0.075
Stand. deviation 1)	3.56	1.56	1.11
t test			
t_{90}	4.92	2.21	1.53
t_{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 *.

TABLE VII
Experimental Design, SS Type
2^5, 1/2 Replicate Factorial Design
with Quadruplicate Center Point

Experiment	Treatments Sulfur (a)	Cure Temp (b)	Mill Setting (c)	Vinsol Conc. (d)	Redicote AP Conc. (e)
I-1	-1	-1	-1	-1	-1
I-2	+1	+1	-1	-1	-1
I-3	+1	-1	-1	+1	-1
I-4	-1	+1	-1	+1	-1
II-1	+1	-1	-1	-1	+1
II-2	-1	+1	-1	-1	+1
II-3	-1	-1	-1	+1	+1
II-4	+1	+1	-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
V-1	-1	-1	+1	-1	+1
V-2	+1	+1	+1	-1	+1
V-3	+1	-1	+1	+1	+1
V-4	-1	+1	+1	+1	+1
III-1	0	0	0	0	0
III-2	0	0	0	0	0
III-3	0	0	0	0	0
III-4	0	0	0	0	0

	Treatment Transforms -1	0	+1	Function
Sulfur (a)[1]	30%	35%	40%	$a=\frac{\%S-35}{5}$
Cure Temperature (b)	280°F	297°F	310°F	$b=\frac{2(\ln F - \ln 297)}{\ln 310-\ln 280}$
Mill Setting (c)	(Three Settings on Pump Speed)			
% Vinsol (d)[2]	1.0	1.3	1.6	$d=\frac{\% V - 1.3}{0.3}$
% Redicote AP (e)[3]	0.0	0.1	0.2	$e=\frac{\% (AP) - 0.1}{0.1}$

1) % of sulfur in SEA
2) Based on Total Emulsion
3) Based upon SEA = 100%

TABLE VIII

DATA and Effects from experimental Design

% Solids and Viscosity

Experiment	Data		Effects				
	% Solids	Brookfield Viscosity 100h, 77°F	Code	% Solids	Significance	Viscosity	Significance
I-1	54.0	31.5	mean	61.84	-	44.5	-
I-2	58.7	38.9	a	1.35	>90%	-2.99	99%
I-3	60.7	35.0	b	0.61*	-	-3.82	>99%
I-4	56.0	27.5	c	2.11	>95%	13.2	≫99%
II-1	61.3	27.5	d	0.66*	-	0.81*	-
II-2	61.5	32.5	e	2.43	>99%	2.74	>95%
II-3	62.1	33.0	ab	0.39*	-	1.44*	-
II-4	62.0	34.5	ac	0.21*	-	-3.17	>99
IV-1	60.0	47.3	bc	0.60*	-	-3.37	>99
IV-2	58.6	53.0	ad	0.39*	-	3.44	>99
IV-3	58.2	63.0	bd	-0.05*	-	-0.06*	-
IV-4	67.5	47.8	cd	0*	-	-0.39*	-
V-1	66.0	83.5	ae	-1.16*	-	-0.99*	-
V-2	67.8	45.3	be	-0.38*	-	-1.37*	-
V-3	66.0	65.7	ce	0.25*	-	2.17*	(>95)
V-4	66.0	55.9	de	-0.73*	-	-0.77*	-
III-1	63.9	35.0	replicate	-1.6*		-0.25*	
III-2	63.5	36.0	replicate	-1.2*		-1.25*	
III-3	60.2	34.0	replicate	2.1*		0.75*	
III-4	61.6	34.0	replicate	0.7*		0.75*	
mean of III	62.3	34.75					
st.dev. of III	1.72	0.96					
			mean dev.	0.049		0.07	
			st. dev.	0.912		1.12	

t Test.

t 90	1.22	1.52
t 95	1.60	2.01
t 99	2.37	3.04

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

TABLE IX. DATA AND EFFECTS FROM EXPERIMENTAL DESIGNS

Settlement (Increase in number indicates decrease in quality).

	Data		Effects				
Experiment	70h Settlement mm	Subjective Settlement	Code	70h Settl.	Signi- ficance	Subj. Assess.	Signi- ficance
I-1	7.6	1 (very slight)	mean	3.45	-	3.0	-
I-2	3.5	1	a	0.03*	-	-0.37*	-
I-3	5.4	1	b	-0.54	> 90%	0.25*	
I-4	3.7	0 (none)	c	-1.18	> 99%	1.75	> 99%
II-1	6.8	1	d	-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*	-
IV-1	3.0	4 (more than slight)	bc	0.53	> 90%	0*	-
IV-2	3.9	8 (very severe)	ad	0.24*	-	0.37*	-
IV-3	3.0	6 (serious)	bd	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 (significant)	ce	-0.19*	-	-0.63	> 95%
V-4	1.4	5	de	0.03*	-	0.37*	-
III-1	3.1	3	replicate	0.3*		-0.33*	
III-2	4.3	3	replicate	-0.9*		-0.33*	
III-3	3.1	4	replicate	0.3*		0.66*	
III-4	3.4	(1) discarded	replicate	0.3*		-	
Mean of III	3.4	3.33					
St. dev. of III	0.6	0.58					
			mean dev. (*group)	0.002		0.025	
			st. dev. (*group)	0.35		0.33	

t test		
t 90	0.47	0.45
t 95	0.62	0.58
t 99	0.94	0.87

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

TABLE X. SS Emulsions of 10% SEA

Code	Formulation, % of Total, Nominal*						Stability				
	Vinsol NVX	Orzan A	Marasperse CE	SPV200 clay	Natrosol 250HR	% solids	off mill	24 hours	Beyond 24 hrs	pH	Notes
20-16B	1.14	0.38	-	-	-	62	yes	yes	yes	10.4	
20-16Ba	1.14	0.38	-	1.0	-	62	yes	yes	yes	10.2	
20-32A	1.14	0.38	-	-	-	-	yes	yes	yes	10.0	1,2
20-44A	1.33	0.38	-	-	-	-	yes	yes	-	10.6	1,2
20-44B	1.33	-	0.38	-	-	-					
20-44C	1.52	0.38	-	-	-	-	yes	yes	-	10.6	1,2
20-45A	1.52	-	0.38	-	-	-	yes	yes	-	10.6	1,2
20-45B	1.71	0.38	-	-	-	-	yes	yes	-	10.6	1,2
20-45C	1.71	-	0.38	-	-	-	yes	yes	yes	10.6	
20-92A	2.8	-	0.9	-	-	53	yes	yes	-	11.5	
20-181:29	2.0	-	0.7	-	0.2	64	yes	yes	-	11.0	3
25-14A	2.38	-	-	-	0.09	66.5	yes	yes	yes	-	4
25-15A	2.38	-	-	-	0.09	67.0	yes	yes	yes	-	5
25-15B	1.98	-	-	-	0.09	67.3	yes	yes	yes	11.2	
25-66A	2.0	=	0.1	-	0.065	60.0	yes	yes	yes	11.0	5 gal sample

Notes

1. Soft Settlement
2. Comparing Orzan A and Marasperse CE, the latter appeared to make a slightly better emulsion.
3. Best emulsion of the series to that time. Natrosol aided greatly.
4. Vinsol added to asphalt the night before, sulfur added 2 hours prior to milling.
5. Vinsol added to asphalt the night before, sulfur added at time of milling.

TABLE XI. RS Emulsions of 10% SEA

Code	Formulation, % of Total, Nominal: Dresinate 731	PAMAK 4	PAMAK 25	PAMAK WCFA	Dresinate TX	Natrosol 250HP	% Solids	Stability: off Mill	24 hrs	Beyond 24 hrs	pH	Notes
20-48A	0.4	-	-	-	-	-	-	yes	no	-	11.2	
20-48B	0.8	-	-	-	-	-	-	yes	no	-	11.2	
20-99A	-	1.0	-	-	-	-	-	yes	yes	no	11.2	
20-99B	-	-	1.0	-	-	-	-	yes	yes	no	11.0	
20-100A	-	-	-	-	1.0	-	-	yes	yes	yes	11.5	
20-100B	-	-	-	1.0	-	-	-	yes	yes	yes	11.0	
20-181-60	-	1.5	-	-	-	-	-	yes	yes	yes	11.0	1
25-12A	-	-	-	0.5	-	0.25	62.8	yes	yes	yes	-	2,3
25-12B	-	-	-	0.75	-	0.24	59.5	yes	yes	yes	-	2,3
25-12C	-	-	-	0.96	-	0.25	62.5	yes	yes	yes	-	2,3
25-66B	-	-	-	0.50	-	0.060	65	yes	yes	yes	-	2,5 ga sample

Notes

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

TABLE XII Emulsions from 10% SEA Base Stocks. CSS

	Formulation											Stability				
Code	Emery 1007	Natrosol 250HR	Indulin W-3	Emery TDA-40	SPV 200 clay	$CaCl_3$	Sherex AA57	Armak E-11	Armak E-63	Jetco AE7	%	mill	24 h	>24 h	pH	Not
20-12A	0.7	-	-	0.5	-	0.1	-	-	-	-	65	yes	no	-	2.9	
20-13A	-	-	-	-	2.0	0.1	1.0	-	-	-	71	no	-	-	3+	
20-14A	-	-	1.0	-	2.0	-	-	-	-	-	-	no	-	-	2.3	
20-53D	-	-	-	-	-	-	3.0	-	-	-	-	yes	no	-	2.2	
20-58B	-	-	-	-	-	-	4.0	-	-	-	-	yes	no	-	2.2	
20-94A	-	-	5.6	-	-	-	-	-	-	-	-	yes	yes	yes	1.5	2
20-94A/C	-	-	5.6	-	0.5	-	-	-	-	-	-	yes	yes	-	1.5	2
20-95A	-	-	-	-	-	-	6.0	-	-	-	-	yes	yes	yes	2.3	3
20-95B	-	-	-	-	-	-	-	3.0	-	-	-	yes	yes	yes	2.2	
20-98A	-	-	-	-	-	-	-	-	3.0	-	-	yes	yes	-	1.5	
20-98B	-	-	-	-	-	-	-	-	-	3.0	-	yes	yes	yes	1.5	
20-183:25	-	0.25	7.0	-	-	-	-	-	-	-	50	yes	yes	yes	1.5	4
25-17A	-	0.065	1.5	-	-	-	-	-	-	-	64	yes	yes	yes	1.5	5,6
25-17B	-	0.064	1.5	-	-	-	-	-	-	-	63	yes	yes	yes	1.5	5,7
25-17C	-	0.065	2.0	-	-	-	-	-	-	-	64.6	yes	yes	yes	1.5	5,6
20-10AB	0.7	-	-	0.5	-	-	-	-	-	-	-	yes	no	-	3,0	1
20-10D	-	-	1.0	-	-	-	-	-	-	-	-	yes	no	-	2.0	
25-66C	-	0.065	2.0	-	-	-	-	-	-	-	60	yes	yes	yes	1.8	8

1) Ran emulsions at natural pH of emulsifiers
2) Clay added to 20-94A with change. Any change observable was detrimental.
3) Increasing the emulsifier content improved stability.
4) After a month this emulsion was still stable.
5) Slight settlement
6) 3% PAMAK WCFA added to sulfur, based on sulfur. 1hr. cure.
7) 3% PAMAK WCFA added to sulfur, based on sulfur. 2hr. cure, allowed to cool and age one week, reheated in oven to 120-140°C before use.
8) 3% PAMAK WCFA added to sulfur, based on sulfur. 2 hr. cure. 5 gallon sample.

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

Code	Tyfo A	Tyfo B	% Solids	Stability mill	Stability 24 h	Stability >24 h	pH	Notes
20-55C	1.5	0.5	62	yes	no	no	2.8	These did not work
20-55D	1.9	0.6	62	yes	no	no	3.0	
20-57B	3.0	1.0	62	yes	no	no	3.6	
20-11C	0.8	0.2	62	no	-	-	3.0	

TABLE XIV. Emulsions from 10% SEA Base Stocks. CRS

Formulations, % of Totals, Nominal

Code	Sherex AA-54	Armak E64	Sherex AA-55	Sherex AA60	Armak E67	Jetco AE6	Natrosol 250HR	% Solids	Stability Mill	Stability 24h	Stability >24h	pH	Notes
20-20A	-	1.0	-	-	-	-	-	70	yes	no	-	2.3	
20-20AC	-	1.0	-	-	-	-	-	70	yes	no	-	2.3	1
20-21A	-	1.0	-	-	-	-	-	70	yes	no	-	3.7	2
20-24B	0.4	-	-	-	-	-	-	68	yes	no		1.6	3,4
20-25A	0.4	-	-	-	-	-	-	68	yes	no		3.6	4
20-27A	0.8	-	-	-	-	-	-	70	yes	no		3.6	5
20-27B	0.8	-	-	-	-	-	-	70	yes	no		2.0	5
20-28A	1.6	-	-	-	-	-	-	70	yes	yes	poor	2.0	
20-30A	2.0	-	-	-	-	-	-	70	yes	yes	yes	3.5	
20-30B	2.0	-	-	-	-	-	-	70	yes	yes	yes	1.2	2
20-102A	1.5	-	-	-	-	-	-	60	yes	no		2.4	
20-102B	-	-	1	-	-	-	-	60	yes	no		2.0	
20-103A	-	-	-	0.78	-	-	-	69	yes	no		2.0	
20-103B	-	-	-	-	0.8	-	-	69	yes	yes	yes	2.0	6
20-104A	-	1.0	-	-	-	-	-	59	yes	yes	yes	2.4	
20-104B	-	-	-	-	-	0.96	-	52	yes	yes	yes	2.5	6
20-183:50	-	-	-	-	1.5	-	0.2	48	yes	yes	yes	1.5	7
20-11B	0.4	-	-	-	-	-	-	68	yes	no	-	2.8	
25-66D	-	-	-	-	1.5	-	0.065	65	yes	yes	yes	2.5	8

1) 1% SPV 200 clay added to 20-20A. It was detrimental.

2) Used $FeCl_3$ as acid

3) 0.1% (on total) $CaCl_2$ added.

4) Soft settlement after 14 hours

5) Experiment to determine whether HCl or $FeCl_3$ might be best acid. HCl was best.

6) E 67 and AE-6 appeared to work the best

7) Vis builder improved emulsion.

8) 3% PAMAK WCFA, based on sulfur, added to the sulfur cured for 2 hrs. min. 5 gal sample

TABLE XV A

Emulsions of 15% SEA Base Stocks. SS Type

	Formulation, % of Total, 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	-	-
20-47B	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

TABLE XV B

Emulsions of 15% SEA Base Stocks. SS Type

	%	Stability				
Code	Solids	Mill	24h	> 24h	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 mill invalidated test			
20-46D	-	-	see 20-46C			
20-47A	-	yes	yes	no	10.5	1
20-47B	61.1	yes	yes	no	10.4	1
20-92B	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
25-50L1	59.2	yes	yes	yes	11.0	4, 5 gallon

1) 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.

TABLE XVI A

Emulsions of 15% SEA Base Stocks. RS Type

Code	Formulation, % of Total, Nominal Dresinate 731	 PAMAK 4	 PAMAK 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	0.7[2]	0.7

TABLE XVI B

Emulsions of 15% SEA Base Stocks. RS Type

Code	% Solids	Stability Mill	 24h	 >24h	pH	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
25-50L20	65	yes	yes	yes	11.0	5 gallon batch excellent

1) Reacted with the sulfur for 2 hours at 275°F.
2) Added to asphalt and neutralized in situ during emulsification.

TABLE XVII A

Emulsions of 15% SEA Base Stocks, CSS Type

Formulation, % of Total, nominal

Code	Indulin W-3	AA-57	E-11	E-63	AE7	NP1007	E-4868	Redicote AP	Natrosol 250HR	PAMAK WCFA	% Solids
20-94B	2	-	-	-	-	-	-	-	-	-	-
20-95A	-	2	-	-	-	-	-	-	-	-	-
20-95B	-	-	3	-	-	-	-	-	-	-	-
20-98A	-	-	-	3	-	-	-	-	-	-	-
20-98B	-	-	-	-	3	-	-	-	-	-	-
20-160	2.0	-	-	-	-	-	-	-	0.2	-	61.4
20-161	2.0	-	-	-	-	-	-	-	-	-	61.4
20-183:25	2.0	-	-	-	-	-	-	-	0.2	-	51.2
25-18:A	1.5	-	-	-	-	-	-	-	0.2	-	62
25-18B	2.0	-	-	-	-	-	-	-	0.2	-	60
25-19A	2.7	-	-	-	-	-	-	0.5	0.1	1.8	64
25-19B	2.7	-	-	-	-	-	-	0.5	0.1	1.8	62
25-37L3	-	-	-	-	-	2	-	-	0.05	0.5	61
25-37L16	2	-	-	-	-	-	-	-	0.05	-	61
25-46L15	2	-	-	-	-	-	-	-	0.1	0.27	60
25-46L16	-	-	-	-	-	-	2	-	0.1	0.27	60
25-47L3	2	-	-	-	-	-	-	-	0.1	0.27	60
25-47L5	-	-	-	-	-	-	2	-	0.1	0.27	60

TABLE XVII B

Emulsions of 15% SEA Base Stocks, CSS Type

Formulation, % of Total, nominal

	Stability				
Code	Mill	24h	>24h	pH	Notes
20-94B	yes	no	-	1.5	Grainy, 85% sediment
20-95A	yes	no	-	2.3	Same as above
20-95B	yes	no	-	2.2	Same as above
20-98A	yes	no	-	1.5	Solidified
20-98B	yes	no	-	1.5	Solidified
20-160	yes	no	-	2.4	Thick layer on surface
20-161	yes	no	-	2.2	Complete Loss
20-183:25	yes	yes	yes	2.0	
25-18:A	yes	no	-	1.5	Failure
25-18B	yes	no	-	1.5	Failure
25-19A	yes	yes	yes	1.5	1, Stable 20 days plus
25-19B	yes	yes	yes	1.5	2, Better than A
25-37L3	yes	no	-	3.2	3,
25-37L16	-	-	-	4.0	Rough Texture
25-46L15	yes	yes	yes?	1.5	4, W-3 better than E4868
25-46L16	yes	yes	no	-	4, Reacting PAMAK first
25-47L3	yes	yes	no	-	3, with sulfur produced
25-47L5	yes	yes	no	-	3, better 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 WCFA reacted with sulfur first, then added to asphalt.

TABLE XVIII A

Emulsions of 15% SEA Base Stocks, CRS Types

Formulation, % of Total, Actual Solids

Code	AA-54	AA-55	AA-60	E-64	Varonic Q230	Varonic T225	E-67	Natrosol 250HR	PAMAK WCFA	% Solids
20-55A	2.0	-	-	-	-	-	-	-	-	-
20-58A	2.5	-	-	-	-	-	-	-	-	-
20-102A	1.0	-	-	-	-	-	-	-	-	60.8
20-102B	-	1.0	-	-	-	-	-	-	-	59.8
20-103A	-	-	0.68	-	-	-	-	-	-	66.0
20-103B	-	-	-	-	-	-	0.78	-	-	69.2
20-104A	-	-	-	0.88	-	-	-	-	-	66.2
20-148A	-	-	-	-	2.0	-	-	0.2	-	-
20-149	-	-	-	-	-	2.0	-	0.2	-	-
20-183-50	-	-	-	-	-	-	1.6	-	-	47.6
25-47L12	-	-	-	-	-	-	2.0	0.06	0.62	-

TABLE XVIII B

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

	Stability				
Code	Mill	24h	>24h	pH	Notes
20-55A	yes	no	-	2.0	Thick layer on top
20-58A	yes	no	-	2.0	Complete failure
20-102A	yes	no	-	2.4	Complete failure
20-102B	yes	no	-	2.0	Complete failure
20-103A	yes	no	-	2.0	Complete failure
20-103B	no	-	-	2.0	Inverted
20-104A	no	-	-	2.0	Inverted
20-148A	yes	no	-	2.0	Complete failure
20-149	yes	no	-	3.0	Complete failure
20-183-50	yes	yes	yes	2.0	After 1 month, non remixable sediment.
25-47L12	yes	yes	yes	2.5	Excellent. Perfect after 16 days. Note 1.

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

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

Formulation, % of Total, nominal

Code	% S in SEA	Vinsol	Orzan A	Marasperse CE	PAMAK WCFA	Natrosol 250HR	TDA-40	Redicote AP	% Solids
20-18B	30	3.0	1.0	–	–	–	–	–	–
20-18Ba	30	3.0	1.0	–	–	–	–	–	–
20-19A	30	3.0	1.0	–	–	–	–	–	–
20-19A/C	30	3.0	1.0	–	–	–	1.0	–	–
20-164A/C	30	2.4	–	–	–	–	1.0	–	–
Factorial I-1	30	1.0	–	–	0.49	0.06	–	0	54
I-4	30	1.6	–	–	0.50	0.06	–	0	56
II-2	30	1.0	–	–	0.55	0.06	–	0.2	61.5
II-3	30	1.6	–	–	0.56	0.06	–	0.2	62.1
IV-2	30	1.0	–	–	0.52	0.06	–	0	58.6
IV-3	30	1.6	–	–	0.52	0.06	–	0	58.2
V-1	30	1.0	–	–	0.60	0.06	–	0.2	66.5
V-4	30	1.6	–	–	0.59	0.06	–	0.2	66.0
III-1	35	1.3	–	–	0.67	0.06	–	0.1	63.9
III-2	35	1.3	–	–	0.67	0.06	–	0.1	63.5
III-3	35	1.3	–	–	0.63	0.06	–	0.1	60.2
III-4	35	1.3	–	–	0.65	0.06	–	0.1	61.6
I-2	40	1.0	–	–	0.70	0.06	–	0	58.7
I-3	40	1.6	–	–	0.73	0.06	–	0	60.7
II-1	40	1.0	–	–	0.74	0.06	–	0.2	61.3
II-4	40	1.6	–	–	0.74	0.06	–	0.2	62.0
IV-1	40	1.0	–	–	0.72	0.06	–	0	60.0
IV-4	40	1.6	–	–	0.81	0.06	–	0	67.5
V-2	40	1.0	–	–	0.81	0.06	–	0.2	67.8
V-3	40	1.6	–	–	0.79	0.06	–	0.2	66.0
20-178A	30	–	–	–	–	0.06	1	–	58.3
25-51C10	30	2.5	–	–	1.34	0.07	–	–	–
25-51C22	40	3.0	–	–	1.74	0.08	–	–	–
25-51C24	40	3.0	–	–	1.74	0.08	–	–	–
25-51C26	40	3.0	–	–	0.74	0.08	–	–	–
25-52-A	40	2.88	–	0.8	0.72	0.07	–	–	65.2

TABLE XIX B.

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

Code	Stability Mill	24h	>24h	pH	Notes
20-18V	yes	yes	-	10.0	Soft sediment in 14 days
20-18Ba	yes	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	yes	-	-	11.8	
Factorial I-1	yes	yes	yes	-	PAMAK WCFA cured in sulfur
I-4	yes	yes	yes	-	and asphalt blend for 2
II-2	yes	yes	yes	-	hours before making emulsions.
II-3	yes	yes	yes	-	See Tables VII and VIII
IV-2	yes	yes	yes	-	for results.
IV-3	yes	yes	yes	-	
V-1	yes	yes	yes	-	" "
V-4	yes	yes	yes	-	" "
III-1	yes	yes	yes	-	" "
III-2	yes	yes	yes	-	" "
III-3	yes	yes	yes	-	" "
III-4	yes	yes	yes	-	" "
I-2	yes	yes	yes	-	" "
I-3	yes	yes	yes	-	" "
II-1	yes	yes	yes	-	" "
II-4	yes	yes	yes	-	" "
IV-1	yes	yes	yes	-	" "
IV-4	yes	yes	yes	-	" "
V-2	yes	yes	yes	-	" "
V-3	yes	yes	yes	-	" "
20-178A	yes	no	-	-	Solidified
25-51C10	yes	yes	yes	-	Note #1,
25-51C22	yes	yes	yes	-	Note #2, settled
25-51C24	yes	yes	yes	-	Note #2, good
25-51C26	yes	yes	no	-	Note #3, unstable
25-52-A	yes	yes	yes	-	Note #4,

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.

TABLE XX

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

	Formulation, % of Total, nominal						Stability				
Code	% sulfur in SEA	PAMAK WCFA in sulfur	PAMAK WCFA in asphalt	Natrosol 250HR	Tergitol 15-5-9	% Solids	mill	24h	>24h	pH	Notes
20-163	30	2.00	-	0.20		65.7	yes	no	-	11.8	
20-166	30	2.00	-	0.10	0.05	-	yes	no	-	10.5	
20-167	30	2.00	-	-	-	-	yes	no	-	10.0	
20-189-2	30	0.6	1.4	-	-	40	yes	yes	yes	11.0	1)Excellent Emulsio
20-190-1	30	0.6	1.4	0.20	-	45.1	yes	yes	yes	10.6	1)Excellent
25-47L15	30	0.54	1.5	0.075	-	-	yes	yes	yes	-	2)Excellent
20-190-3	40	0.8	1.2	0.20	-	45	yes	yes	yes	10.4	1)3) Excellent
20-190-2	40	0.8	1.2	0.20	-	53	yes	yes	yes	10.6	1)Excellent
25-51-C20	40	0.74	2.4	0.06	-	-	yes	yes	yes	-	2)Excellent

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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. PAMAK WCFA cured 2 hours in sulfur before adding sulfur to blend of asphalt and remaining PAMAK WCFA. 5 gallon sample.

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

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

Formulation % on Total, Nominal Except as Noted

	% sulfur in SEA	Indulin W-3	AA-57	E-11	E-63	AE-7	PAMAK WCFA	Redicote AP	Natrosol 250HR	% Solids
20-94C	30	2.0	-	-	-	-	-	-	-	-
20-95A	30	-	6.00	-	-	-	-	-	-	-
20-95B	30	-	-	3.0	-	-	-	-	-	-
20-98A	30	-	-	-	3.0	-	-	-	-	-
20-98B	30	-	-	-	-	3.0	-	-	-	-
25-21-(-)	30	2.24 1)	-	-	-	-	1.36 1)	0.68 1)	0.048 1)	68
a	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
c	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
ad	40	2.24	-	-	-	-	0.67	0.67	0.099	67
bd=f	30	2.24	-	-	-	-	1.34	0.34	0.099	67
abd	40	2.45	-	-	-	-	1.30	0.33	0.105	65
cd	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
abcd	40	3.78	-	-	-	-	1.28	0.65	0.108	64
25-5A	40	2.01	-	-	-	-	-	0.51	0.19	51.4

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.

TABLE XXI B

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

Code	Stability			pH	Notes
	mill	24h	>24h		
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
c	yes	no	-		Rapid Distress
ac	yes	no	-		Rapid Distress
bc=e	yes	no	-		Slow break
abc	yes	no	-		Better than e
d	yes	yes	no		Appeared like cottage cheese, could be mixed with H_2O.
ad	yes	no	--		Broke
bd=f	yes	yes	no		Paste, however adding water would make emulsion.
abd	yes	no	-		Distress after awhile, better than ab, c or ac.
cd	yes	no	-		
acd	yes	no	-		
bcd	yes	yes	yes		Not perfect, but good
abcd	yes	no	-		
25-5A	yes	no	-		Failed in about 30 min.

TABLE XXII A. Emulsions of Sulphlex

Formulation, % of Total, Nominal

	Type of Sulphlex	Type of of Emulsion	Bentonite clay	Redicote E-11	Orzan A	Natrosol 250HR	PAMAK WCFA	Emery G 752	Indulin W-3
20-125A	CDC soft	clay	2.5	-	-	-	-	-	-
20-125B	CDC soft	clay	4.0	0.1	2.0	-	-	-	-
20-130	CDC soft	RS	-	-	-	0.1	2.0	-	-
20-134B	CDC soft	clay-CSS	2.0	-	0.9	-	-	-	1.96
20-134A	CDC soft	clay	-	-	-	-	-	2.0	-
20-135	CDC soft	clay	-	0.3	2.5	-	-	-	-

			TDA 40	Indulin W-2	Varion[1] CAS	Natrosol 250HR	PAMAK WCFA	NP 1007	Indulin W-3	Redicote AP	Redicote E-67	% Solids
20-178B	CDC soft	RS	1.0	-	0.5	0.2	1.0	-	-	-	-	53.2
20-178C	CDC soft	SS	1.0	-	1.0	0.2	-	-	-	-	-	52.8
20-188-1	CDC soft	RS	-	-	-	0.2	1.0	-	-	-	-	34.0
20-188-2	#61.5 hard	RS	-	-	-	0.2	1.0	-	-	-	-	-
20-188-3	CDC soft	SS	-	-	2.0	0.2	-	-	-	-	-	27
20-188-4	#61.5 hard	MS?	-	-	-	0.2	2.0	2.0	-	-	-	43.2
25-2A	CDC soft	CSS	-	-	-	-	-	-	2.0	1.0	-	-
25-2B	CDC soft	CRS	-	-	-	0.25	-	-	-	1.0	2.0	41
25-3A	CDC soft	CRS	-	-	-	0.27	-	0.5[5]	-	-	2.0[5]	32.9
25-3B	CDC soft	CSS	-	4.0[5]	-	0.27	-	0.5[5]	-	-	-	38.5

1) Coco Sulfobetaine
5) Based on Sulphlex. Added to Sulphlex and reacted one hour. Reaction appeared to be excellent.

TABLE XXII B. Emulsions of Sulphlex

	Stability				
Code	mill	24h	>24h	pH	Notes
20-125A	yes	yes	yes	2	Excessive shot & broke in a few days.
20-125B	yes	yes	yes	3.5	Excellent
20-130	no	no	no	11.2	Emulsion didn't make. Waring Blender
20-134B	no	no	no	11	Failed
20-134A	no	no	no	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	-	Lasted 4 days.
20-188-1	yes	yes	yes	10.5	Excellent 2)
20-188-2	no	no	no	-	Did not make.
20-188-3	yes	yes	no	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	no	-	-	
25-3B	yes	no	-	-	

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.

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 cellulose viscosity builder.
Dresinate 731	Hercules	Anionic RS emulsifier. Rosin Soap
PAMAK 4	Hercules	Anionic RS emulsifier, tall oil.
PAMAK 25	Hercules	Anionic RS emulsifier, tall oil.
PAMAK WCFA	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-40	Emery	Nonionic, CSS emulsifier, 40 mole ethoxylated tridecylalcohol.
Arosurf AA-57	Sherex Chemical Company P.O. Box 646 Dublin, Ohio 43017	Cationic, CSS emulsifier, amine

A-2

Ingredient	Manufacturer	Type
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	Emulsifier, 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	Emulsifier, coco sulfobetaine
G-752	Sherex	Emulsifier, ethoxylated amine

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 commercially, especially the CRS type. CRS emulsions are applied hot, thus an emulsion that is not stable at 140-170°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.

TABLE I. Emulsion Formulations of 15% Sulfur Extended Asphalt Base Stocks. Effect of Storage Temperature.

		CSS Emulsifiers							CRS Emulsifier			
Formulation, Nominal	I	Ia	Ib	Iab	II	IIa	IIb	IIab	III	IIIa	IIIb	IIIab
Asphalt Husky AC20	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0	51.0
Sulfur	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	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	-	-	-	-	-	-	-	-
AA57	-	-	-	-	2.0	2.0	2.0	2.0	-	-	-	-
AA54	-	-	-	-	-	-	-	-	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
HCl 35% conc.	-	-	-	-	-	-	-	-	0.8	0.8	0.8	0.8
Properties												
Solids	65	65	66	65	62	61	64	63	64	64	64	59
Stability, Room Temp.	fail	OK	poor	OK	fail	poor	fair	satisfactory	fail	satisfactory	good	good
140°F	failed	failed	failed	failed	failed	failed	failed	failed	fail	poor	poor	poor

Comments

1) Sustained temperature of 140°F for 16 hr cause an accelerated degradation of emulsion quality compared with naturally or rapidly cooled samples.

2) Emulsion quality improved as the level of surface active compounds increased to the limits of the experiment.

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

	40 SEA		30 SEA		15 SEA	10 SEA	15 SEA		10 SEA	
	CRS	CSS	CRS	CSS	CSS	CSS	CSS	CRS	CSS	CRS
	29-26A	29-26C	29-26B	29-26D	29-27	29-27B	29-29A	29-29C	29-29B	29-29D
Asphalt, Husky AC20	36.0	36	42.0	42.0	51.0	54.0	51.0	51.0	54.0	54.0
Sulfur	24	24	18	18	9.0	6.0	9.0	9.0	6.0	6.0
PAMAK WCFA	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
Tomah TAE-DR (75)	-	2.0	-	2.0	-	-	-	-	-	-
Sherex AA57	-	-	-	-	2.0	2.0	2.0	-	2.0	-
Sherex AA54	2.0	-	2.0	-	-	-	-	2.0	-	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	0.8	0.001	0.8
Batch Size	1 qt	1 qt	1 qt	1 qt	5 gal	5 gal	4 x 1qt	4 x 1qt	4 x 1qt	4 x 1qt
Properties										
Measured % Solids	55	55	52	53	60	57	54	57	56	61
Stability	failed	failed	failed	failed	failed	failed	good	good	good	good

Comments

For improved results the factors below should be noted:

1) The emulsions should be cooled as soon as possible after milling.
2) Mechanical action upon the emulsions especially when hot accelerates breaking.
3) PAMAK and Redicote must be added to the sulfur and asphalt respectively but the blend of the two should not be made until just prior to emulsification.

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

CO_2 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

1. Assemble apparatus. A schematic of the assembled apparatus is shown in Figure B10.

2. 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.

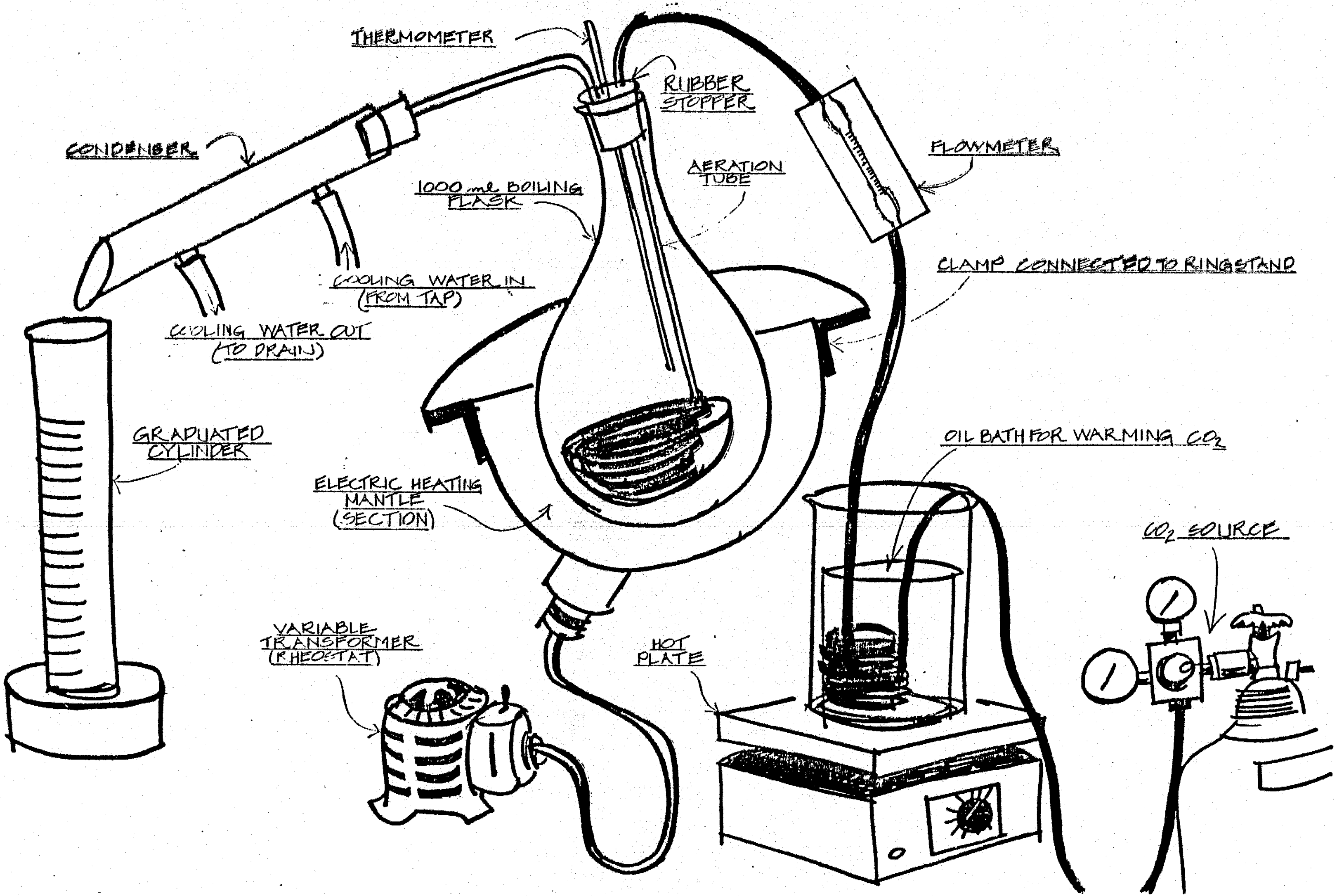


FIGURE 10 Schematic Diagram of Modified Distillation Apparatus

APPENDIX C
PHYSICAL PROPERTIES OF EMULSIONS

TABLE 12 Water Content by Distillation; %

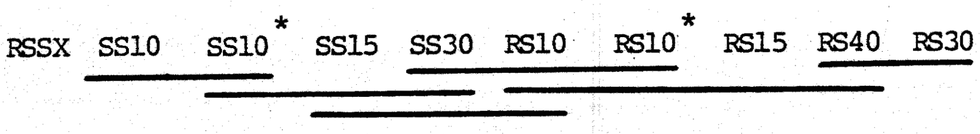
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	40.8	34.9	39.9	34.6	38.0	34.3	37.8	29.4	33.1	-	-	-	-	45.4
	39.9	35.1	41.2	35.8	37.9	33.7	37.9	30.0	32.5	-	-	-	-	48.9
X	40.3	35.0	40.5	35.2	37.9	34.0	37.8	29.7	32.8	-	-	-	-	47.1
s	0.8	0.2	1.2	1.1	0.1	0.5	0.1	0.5	0.5	-	-	-	-	3.1
Cv	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	F.01
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 by Distillation

TABLE 14 Water Content by Evaporation; %

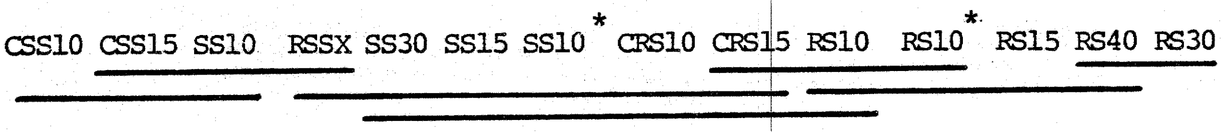
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	37.1 40.5	35.1 34.6	41.0 41.2	36.5 36.4	39.7 38.0	34.1 33.5	38.0 39.9	30.2 30.1	32.4 33.8	42.0 43.3	38.5 38.3	42.1 42.3	37.6 38.4	40.9 39.6
X	38.8	34.8	41.1	36.4	38.8	33.8	38.9	30.1	33.1	42.6	38.4	42.2	38.0	40.2
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
Cv	7.7	1.1	0.5	0.3	3.9	1.5	4.4	0.3	3.6	2.8	0.5	0.5	1.8	3.0

$q_{crit} = 0.522$ $q = 0.266$

*Note: PAMAK WCFA not reacted with sulfur.

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

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



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

TABLE 16 Storage Stability; %

	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	-0.1	-	0.7	0.1	0.6	-0.2	0.0	-1.1	30.7	-	-	-	-	59.6
	1.3	-	0.3	0.5	-0.1	0.5	0.4	-0.3	35.8	-	-	-	-	60.4
X	0.6	-	0.5	0.3	0.25	0.15	0.20	-0.7	33.3	-	-	-	-	60.0
s	1.2	-	0.4	0.4	0.62	0.62	0.4	0.7	4.5	-	-	-	-	0.7
Cv	207	-	70.9	118	248	413	177	101	13.6	-	-	-	-	1.2

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

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 17 One-Way ANOVA Summary, Storage Stability

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

RSSX RS40 SS10* 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 Freeze Thaw Resistance

	Replication 1			Replication 2		
Emulsion	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
SS 10*	H**	H	H	H	H	H
RS 10*	B	B	B	B	B	B
SS 10	H	H	H	H	H	H
RS 10	B	B	B	B	B	B
SS 15	B	B	B	B	B	B
RS 15	H,T	B	B	H,T	B	B
SS 30	B	B	B	B	B	B
RS 30	H	H,T	H,T	H	H	H,T
CSS 10	B	B	B	B	B	B
CRS 10	B	B	B	B	B	B
CSS 15	B	B	B	B	B	B
CRS 15	B	B	B	B	B	B
RS SX	B	B	B	B	B	B

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

TABLE 19 Emulsion Break Time; min

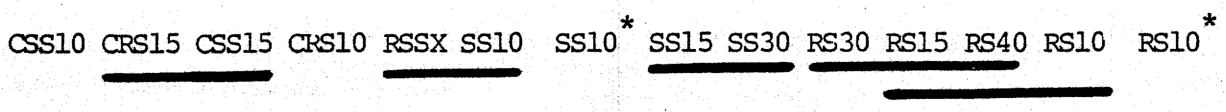
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	15.0	0.5	18.5	4.0	11.0	5.5	11.5	5.5	5.0	40.0	24.0	30.0	30.0	20.0
	16.5	0.5	18.5	4.2	13.0	6.0	10.8	6.7	6.0	38.5	22.0	30.0	31.0	20.0
X	15.8	0.5	18.5	4.1	12.0	5.8	11.2	6.1	5.5	39.3	23.0	30.0	30.5	20.0
s	1.3	0.0	0.0	0.2	1.8	0.4	0.6	1.1	0.9	1.3	1.8	0.0	0.9	0.0
Cv	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	F.01
Mixture	13	3505.1	269.6	451.5	2.43	3.87
Error	14	8.4	0.60			
Total	27	3513.5				



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

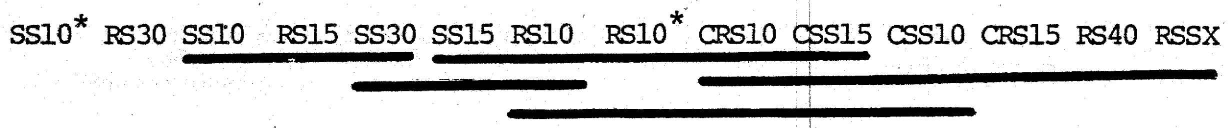
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	239	45.2	71.7	45.0	45.8	74.9	65.6	121	20.2	25.9	31.7	28.0	25.8	18.8
	213	44.0	72.7	44.0	45.0	66.4	67.5	140	20.1	27.3	31.5	28.2	26.3	19.3
X	226	44.6	72.2	44.5	45.4	70.7	66.6	13.1	20.2	26.6	31.6	28.1	26.1	19.1
s	23.0	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

$q_{crit} = .522$ $q = .473$

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 22 One-Way ANOVA Summary, Saybolt Fural Viscosity

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



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[1]

Emulsion Designation	Replication	Dry Aggregate Initial Coating	Dry Aggregate Coating After Rinse	Wet Aggregate Initial Coating	Wet Aggregate Coating After Rinse
SS 10*	1	G[2]	P	G	G[3]
	2	G	P	G	P
SS 10	1	G	P	G	P
	2	G	P	G	P
RS 10	1	G	P	P	P
	2	F	P	P	P
SS 15	1	G	P	G	P
	2	G	P	G	P
RS 15	1	G	G	P[4]	P[3]
	2	G	G	P[4]	P
SS 30	1	G	P	G	P
	2	G	P	G	P
RS 30	1	G	F	G	F
	2	G	F	G	F
RS 40	1	G	P	G	P
	2	G	P	G	P
CSS 10	1	G	P	G	P
	2	G	P	G	P
CRS 10	1	G	F	G	G
	2	G	F	G	G
CSS 15	1	G	P	G	F
	2	G	P	G	P
CRS 15	1	G	F	G	G
	2	G	F	G	G
RS SX	1	G	P	G	P
	2	G	P	G	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.

TABLE 24 Water Miscibility, Maximum Difference; %

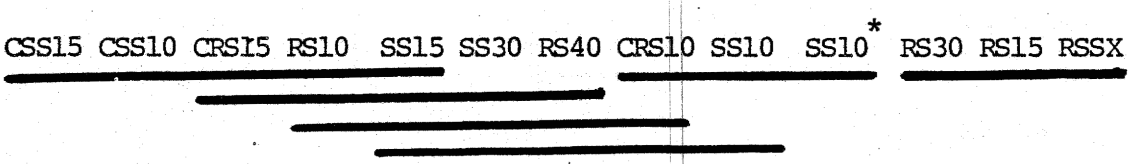
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	26.8	-	32.2	42.7	47.1	10.6	32.4	10.5	35.7	50.4	37.0	52.3	46.4	10.0
	28.2	-	37.9	47.4	39.5	9.4	45.9	12.5	37.6	50.9	35.3	51.3	46.3	9.1
X	27.5	-	35.1	45.1	43.3	10.0	39.2	11.5	36.7	50.7	36.2	51.8	46.4	9.6
s	1.2	-	5.1	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

*Note: PAMAK WCFA not reacted with sulfur.

TABLE 25 One-Way ANOVA Summary, Water Miscibility

Source	df	SS	MS	F	F.05	F.01
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; %

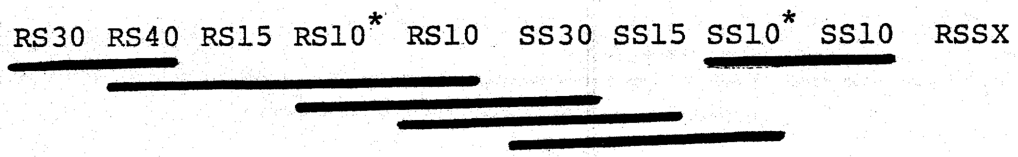
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	59.2	65.1	60.1	65.4	62.0	65.7	62.2	70.6	66.9	-	-	-	-	54.6
	60.1	64.9	58.8	64.2	62.1	66.3	62.1	70.0	67.5	-	-	-	-	51.1
X	59.7	65.0	59.5	64.8	62.1	66.0	62.2	70.3	67.2	-	-	-	-	52.9
s	0.8	0.2	1.2	1.1	0.1	0.5	0.1	0.5	0.5	-	-	-	-	3.1
Cv	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	F	F.05	F.01
Mixture	9	431.2	47.91	55.30	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 17 Newman-Keuls Ranking, Residue Content by Distillation

TABLE 28 Residue Content by Evaporation; %

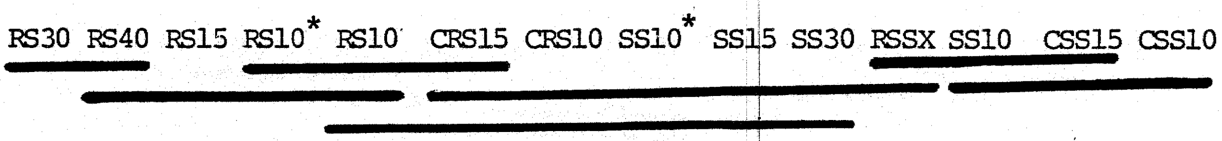
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	62.9	64.9	59.0	63.5	60.3	65.9	62.0	69.8	67.6	58.0	61.5	51.9	62.4	59.1
	59.5	65.4	58.8	63.6	62.0	66.5	60.1	69.9	66.2	56.7	61.7	57.7	61.6	60.4
X	61.2	65.2	58.9	63.6	61.2	66.2	61.1	69.9	66.9	57.4	61.6	57.8	62.0	59.8
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
Cv	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 29 One-Way ANOVA Summary, Residue Content by Evaporation

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



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

TABLE 30 Demulsibility; %

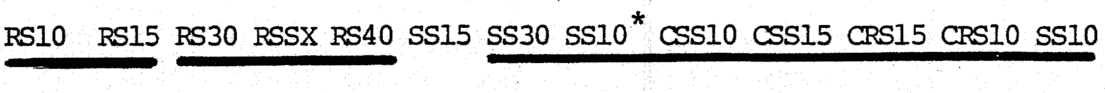
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	0.8	-	0.0	71.6	10.3	70.2	0.7	33.5	32.5	0.5	0.2	0.3	0.2	30.3
	0.2	-	0.0	80.2	10.8	68.0	0.8	35.7	24.7	0.4	0.2	0.3	0.2	32.1
X	0.5	-	0.0	75.9	10.6	69.1	0.8	34.6	28.6	0.5	0.2	0.3	0.2	31.2
s	0.5	-	0.0	7.6	0.4	1.9	0.1	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	F.01
Mixture	12	17476.3	1456.4	255.24	2.62	4.00
Error	13	74.2	5.71			
Total	25	17550.5				



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

FIGURE 19 Newman-Keuls Ranking, Demulsibility

TABLE 32

LONG TERM STABILITY OF SEA AND SULPHLEX EMULSIONS

Emulsion	Time[1] (Months)	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 separation and small asphalt globules present
CRS 15	1.5	Good, slight settlement
RS Sulphlex	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

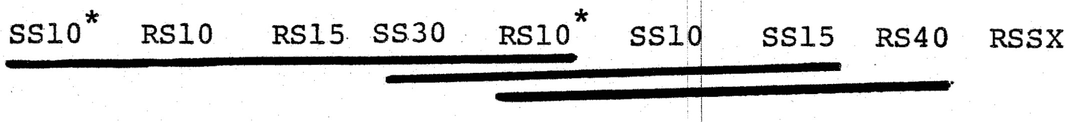
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	128	88	62	111	75	120	111	-	67	-	-	-	-	9
	99	83	88	114	70	105	90	-	62	-	-	-	-	6
X	114	86	75	113	73	113	101	-	65	-	-	-	-	8
s	25.7	4.4	23.0	2.7	4.4	13.3	18.6	-	4.4	-	-	-	-	2.7
Cv	22.6	5.2	30.7	2.4	6.1	11.8	18.5	-	6.9	-	-	-	-	35.4

$q_{crit} = .750$ $q = .273$

*Note: PAMAK WCFA not reacted with sulfur.

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

Source	df	SS	MS	F	F.05	F.01
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 Distillation, 140F; Poise

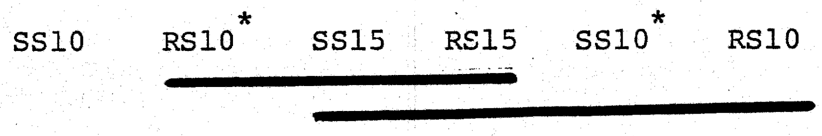
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	729	919	1601	816	977	867	-	-	-	-	-	-	-	-
	890	1183	1711	799	940	824	-	-	-	-	-	-	-	-
X	810	1051	1656	808	959	846	-	-	-	-	-	-	-	-
s	143	234	97	15	33	38	-	-	-	-	-	-	-	-
Cv	17.6	22.3	5.9	1.9	3.4	4.5	-	-	-	-	-	-	-	-

q_{crit} = .949 q = .460

*Note: PAMAK WCFA not reacted with sulfur.

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

Source	df	SS	MS	F	F.05	F.01
Mixture	5	1.06-E06	2.12-E05	22.84	4.39	8.75
Error	6	.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

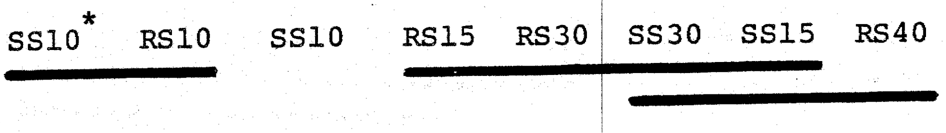
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS 30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	100	-	64	100	31	37	38	30	23	-	-	-	-	-
	100	-	72	100	34	44	30	43	27	-	-	-	-	-
X	100	-	68	100	33	41	34	37	25	-	-	-	-	-
s	0.0	-	7.1	0.0	2.7	6.2	7.1	11.5	3.5	-	-	-	-	-
Cv	0.0	-	10.4	0.0	8.2	15.3	20.8	31.6	14.2	-	-	-	-	-

$q_{crit} = .793$ $q = .286$

*Note: PAMAK WCFA not reacted with sulfur.

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

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



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

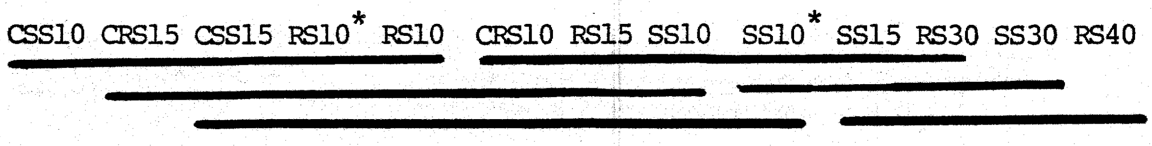
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	91	107	87	107	84	70	50	65	61	149	87	113	128	-
	76	128	96	114	66	119	81	69	50	147	108	122	129	-
X	84	118	92	111	75	95	66	67	56	148	98	118	129	-
s	13.3	18.6	7.9	6.2	15.9	43.4	27.5	3.5	9.7	1.8	18.6	8.0	0.9	-
Cv	15.9	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	df	SS	MS	F	F.05	F.01
Mixture	12	17854	1487.9	7.52	2.63	4.00
Error	13	2573	197.9			
Total	25	20427				



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 Evaporation, 140F; Poise

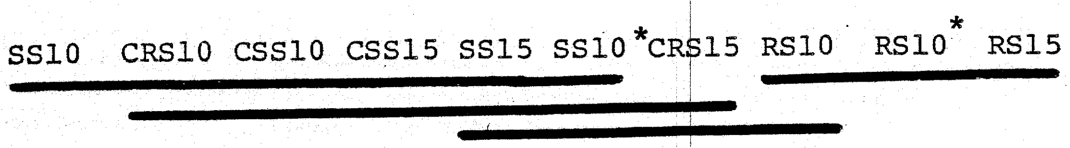
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	1325	640	1636	708	1261	645	-	-	-	1560	1541	1364	1284	-
	1055	762	2111	791	1194	727	-	-	-	1140	1850	1281	1085	-
X	1190	701	1784	750	1228	686	-	-	-	1350	1696	1323	1185	-
s	239	108	420	74	59	73	-	-	-	372	274	74	176	-
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	df	SS	MS	F	F.05	F.01
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				



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

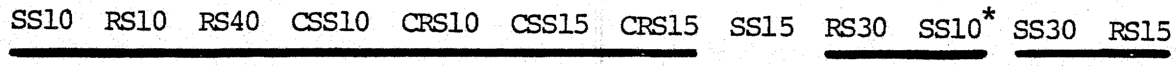
	SS 10*	RS 10*	SS 10	RS 10	SS 15	RS 15	SS30	RS 30	RS 40	CSS10	CRS10	CSS15	CRS15	RS SX
DATA	38	-	100	100	47	18	16	35	100	100	100	100	100	-
	28	-	100	100	46	18	23	39	100	100	100	100	100	-
X	33.0	-	100	100	46.5	18	19.5	37.0	100	100	100	100	100	-
s	8.9	-	0.0	0.0	0.9	0.0	6.2	3.5	0.0	0.0	0.0	0.0	0.0	-
Cv	26.8	-	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	F	F.05	F.01
Mixture	11	29096	2645	382.43	2.72	4.23
Error	12	83	6.92			
Total	23	29179				



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

Report No. FHWA/RD-80/191

ENVIRONMENTAL AND SAFETY ASPECTS OF THE USE OF SULFUR IN HIGHWAY PAVEMENTS

Volume 1 - Evaluation of Environmental and Safety Hazards

September 1980
Final Report

FEDERAL HIGHWAY ADMINISTRATION
OFFICES OF RESEARCH & DEVELOPMENT
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16. Abstract

The use of sulfur in highway paving mixtures has introduced questions regarding the pollutants generated, their environmental impact and the safety aspects associated with mix preparation and placement. This report presents the results of an investigation in which these factors are assessed.

The study considered the safety and environmental aspects of storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur. These considerations included possible evolution of toxic and abnoxious fumes, dust and runoffs. Results of tests simulating in-service conditions such as traffic wear, skidding, freeze thaw, spills and fires are also discussed. The effects of these pollutants on humans, soils, highway structural materials, ground waters and vegetation is presented. Along with the laboratory study a detailed work plan which discusses methods and equipment for monitoring potential emissions and pollutants and recommended safety practices was generated. An annotated bibliography dealing with the safety and environmental effects on sulfur-modified paving materials was also prepared.

The final report was prepared in three volumes: Volume I - Evaluation of Environmental and Safety Hazards; Volume II - Field Evaluation Plan and Volume III - Annotated Bibliography.

17. Key Words
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1 INTRODUCTION

1.1 Background

1.1.1 Sulfur - Asphalt Paving Mixtures.

Since 1973, the Texas Transportation Institute (TTI) has been actively engaged in a number of studies related to the use of sulfur in asphaltic pavement mixtures. Sulfur is unique in that it is one of the few materials which is expected to be in ample supply in the future. The primary reason for this potential over-supply is attributed to pollution abatement controls targeted at power plant stack gas emissions and the expected growth of recovered (secondary) sulfur supplies following commercialization of processes for synthetic natural gas, coal liquification, shale oil and other alternative energy sources. The present inventory of pollution abatement sulfur is increasing at a rate of about 4 million tons per year and it is predicted that by the latter part of this decade the supply will begin to exceed the demand. For this reason a considerable amount of research and development has been initiated to find uses for sulfur. One of the most promising areas being studied is in asphaltic pavement mixtures.

Depending on the manner in which it is introduced into the mix, sulfur can be used as a structuring agent (i.e. playing the role of an aggregate) in upgrading poorly graded sands or as an integral part of the binder in the form of sulfur-asphalt dispersions.

The first concept was pioneered by Shell Canada Ltd. [1-4] and resulted in a patented sand-asphalt sulfur (S-A-S) mix called Thermopave [5]. In S-A-S mixtures molten sulfur is added to asphalt at a sulfur/asphalt weight ratio, S/A, of 2 to 1. Sulfur fills the interstitial voids around the aggregate particles which, upon cooling, creates a mechanical interlock from which the material derives its strength. Developed primarily for use in areas where quality aggregates are scarce, S-A-S mixes prepared using locally available dune sands and beach sands have been shown to have performance characteristics equal to and in some cases superior to quality asphaltic concrete mixtures.

The Texas Transportation Institute (TTI) under the sponsorship of The Bureau of Mines and The Sulphur Institute [6] are currently extending the technology developed in Canada for application in the United States. This project started in 1973 and resulted in the successful placement of the first major domestic field test of Thermopave. The test section was a two-lane, 3000 ft (914 m) long, variable thickness pavement built on U. S. 77, south of Corpus Christi, Texas during April, 1977 [7]. This pavement is now in the third year of a post-construction evaluation. TTI participated in another Thermopave trial in Sulfur, Louisiana which took place during January 1977. This test section was 2000 ft. (610 m) in length and 24 ft (7.3 m) wide.

Considerable uncertainty about the future availability and cost of asphalt cement has been generated by the current energy squeeze and pricing as established by foreign suppliers. This has initiated considerable research activity in the United States [8, 9, 10], Europe [11] and Canada [12] directed to the partial or total replacement of the asphalt as the binder in asphaltic concrete. To this end, processes using sulfur as a substitute for up to 50 percent of the asphalt in asphaltic concrete mixtures are making inroads in the United States. These processes have been both developed and demonstrated independently by Societe' Nationale des Petroles d'Aquitaine (SNPA)* in France [11] and Gulf Oil Canada [12] using sulfur-asphalt "preblending" techniques and equipment which are proprietary to each. TTI, under the sponsorship of SNPA and The Sulphur Institute, conducted a series of

---

*Currently Societe Nationale Elf d'Aquitaine (SNEA) verification studies using the SNPA process which culminated in a 3,650 ft. (1113 m) long, two-lane test section on U. S. 69 near Lufkin, Texas [13]. The test binder was a sulfur-asphalt blend in which 30 percent of the weight of the binder (i.e., 15 volume percent) consisted of sulfur. Gulf Canada has reported the placement of pavement mixtures with 50 weight percent sulfur in the binder [12].

In a cooperative effort with the Bureau of Mines' Metallurgy Research Laboratory in Boulder City, Nevada, TTI has been investigating paving mixtures which are prepared using "direct" mixing of the sulfur and asphalt [10]. This method would eliminate the need for specialized high shear-rate colloid mills or emulsifiers as proposed by Gulf and SNPA. During January 1977, a trial section of pavement using this concept was constructed in conjunction with the Nevada Highway Department on a portion of US 95 near Boulder City, Nevada. This pavement is also under post-construction evaluation by TTI for the Bureau.

Another SEA field trial took place in Bryan, Texas [14] in 1979 in which mixes prepared by both the "preblending" process and the Bureau of Mines' "direct" mixing process were utilized. The test section consisted of two lanes, 2,700 ft. (824 m) long and located on MH 153 in Brazos County, Texas.

TTI was also being sponsored by the Federal Highway Administration to carry out an extensive investigation to utilize sulfur as an asphalt extender [9]. This program studied a wide variety of asphalt cements and aggregates to generate and optimize mix design rationale in which asphalt demand is reduced by the use of sulfur.

An additional approach for the use of sulfur in road and highway construction is in the area of recycling old bituminous pavements [10,15]. This concept was conceived and is being developed as part of the TTI-Bureau of Mines cooperative effort. Only laboratory data has been generated at this time, but plans are being formulated to construct a field demonstration sometime during 1981. One successful sulfur-recycled pavement was constructed by the Minnesota Highway Department near Minneapolis during 1979 [16]. Most of the conventional asphalt pavement recycling processes require the use of some type of softening agent to peptize the age-hardened asphalt in the old pavement [17]. Sulfur has the ability to reduce the viscosity of sulfur-asphalt dispersions below that of the virgin asphalt [11, 12] at normal mix temperatures and to increase the stiffness of the sulfur-asphalt-aggregate mixtures when it cools. This characteristic is being investigated for city and urban streets where cut-backs have a tendency to produce mixtures with low stiffnesses.

A current on-going FHWA sponsored research program at TTI is studying the use of sulfur-extended asphalt (SEA) binder in open-graded friction courses (OGC) [18]. This project will produce a mix design procedure specifically oriented to sulfur-asphalt mixes. An experimental field demonstration project to construction an SEA-OFC pavement near Nacogdoches, Texas, was completed during the summer of 1980. The project utilized a dryer drum plant for preparing the mixes.

1.1.2 Sulfur Concrete Mixes

Mixes prepared without the use of asphalt are called sulfur concretes. Studies conducted by Southwest Research Institute [19] and the Bureau of Mines [20] have shown that sulfur concretes can be made with compressive strengths equal to or superior to portland cement concrete with an added capability of reaching full strength within hours. SWRI studies were generated primarily to develop a building material whereas the Bureau of Mines activity dealt primarily with the fabrication of acid resistant holding tanks and retaining walls.

When molten sulfur, which has been mixed with aggregate, solidifies and cools it undergoes an allotropic change from monoclinic to orthorhombic form. Orthorhombic sulfur being denser and smaller in unit volume than monoclinic brings about a high degree of shrinkage which creates high internal stresses. This renders the sulfur concrete susceptible to freeze-thaw deterioration. This has been partially overcome through the use of glass fibers or pumice as an intermediate filler and plasticizers such as dicyclopentadiene (DCPD) Dipentene (DP), etc.

Field tests on sulfur concrete slabs using 5% DCPD significantly out-performed the unmodified sulfur concrete in its resistance to weathering and temperature fluctuations. The flexural strength of modified sulfur concrete range from 18-25% of the compressive strength as compared to 10-15% of the compressive strength for straight sulfur and pcc materials.

1.1.3 Sulfur and Sulfur-Asphalt Chemistry

Elemental sulfur in its pure form is a yellow, crystalline solid. The melting/freezing point of sulfur is around 240°F (116°C), subject to its previous history and on its rate of heating and cooling [21, 22]. The heat of fusion is about 21.6 Btu/lb. (12 cal/g) [22]. Above the melting point, sulfur is a thin liquid up to about 320°F (160°C), after which the viscosity abruptly increases making pumping difficult [21, 23]. Figure 1 shows the viscosity of sulfur versus temperature. Liquid sulfur is normally handled at a temperature range 270 to 300°F (132 - 149°C) [21]. Within this range, it is not corrosive to steel or aluminum unless trapped water or acid is present [21, 24, 25]. Above 320°F (160°C), toxic gases form and increase as temperature continues to rise. In general, the amount of hydrogen sulfide (H_2S) generated is higher as the hydrocarbon content of the sulfur increases. The flash point of sulfur ranges from 335 to 370°F (169 to 188°C) [21, 26, 27] compared with 340 to 600°F (171 to 316°C) of asphalt cement. The auto ignition temperature of sulfur is around 500°F (260°C) [21, 28]. Sulfur is not soluble in water, but is moderately soluble in many other liquids [29] including asphalt.

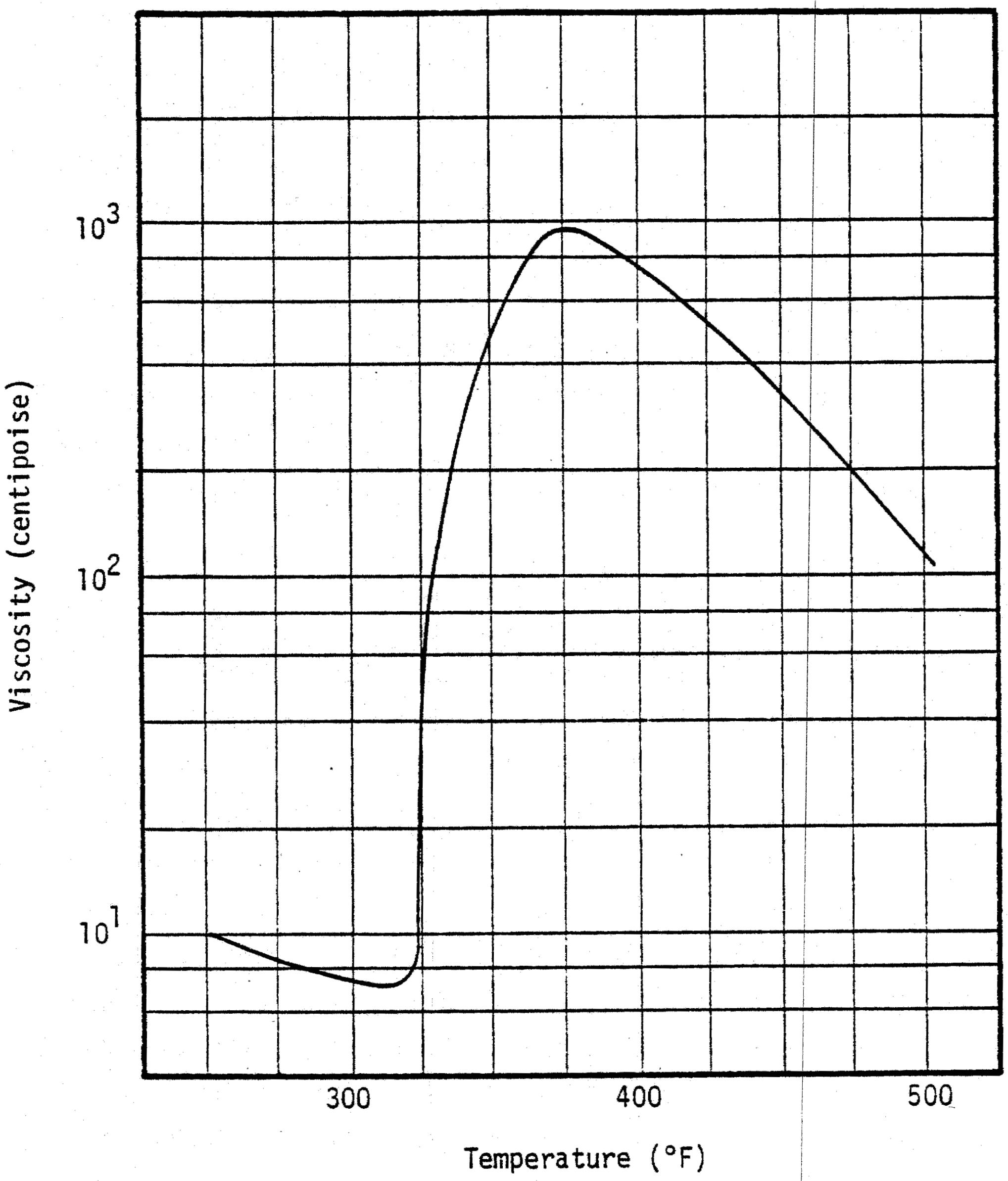


Figure 1 . Viscosity-Temperature Curve for Liquid Sulphur

°C = (°F - 32) x 5/9

The thermal conductivity of sulfur modified pavement mixes vary widely with composition. One series of tests found nearly comparable values for Sulfur-Asphalt-Sand (SAS) pavement systems and asphalt concrete of 11.7 and 15.7 x 10^{-4} cal/cm^2 - sec - °C, respectively [30].

The primary hazards due to the presence of sulfur in pavement operations and handling situations are gaseous emissions of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) as well as airborne fumes and particulate (colloidal) sulfur. These primary hazards can usually be gauged in terms of temperature, time-duration under temperature, and dispersion factors. The relative toxicity of these pollutants will be discussed later in this report.

The sulfur-asphalt mixes are prepared using elemental sulfur and asphalt preheated to temperatures ranging from 265 to 300°F (130 - 149°C). Under these conditions the elemental sulfur can be oxidized to sulfur dioxide, which in turn can be converted to sulfur trioxide (Eqn 1).

$$(1) \qquad \frac{1}{8}S_8 \xrightarrow{\text{air}} SO_2 \xrightarrow{\text{air}} SO_3$$

The oxidation of sulfur dioxide to sulfur trioxide is rather slow in the absence of catalysts. In the presence of moisture these two oxides of sulfur will dissolve in any water droplets present. Sulfur dioxide, which is quite soluble in water, will be physically dissolved in the droplets with an exceedingly small part reacting with the water to form sulfurous acid (Eqn 2).

$$(2) \qquad SO_2 \xrightarrow{H_2O} SO_2 \text{ dissolved} \xrightarrow{H_2O} H_2SO_3$$

Aqueous solutions of sulfur dioxide possess acidic properties with a dissociation constant of 1.3 x 10^{-2} ascribed to the medium-strong sulfurous acid.

Sulfur trioxide will form the strong and corrosive sulfuric acid (Eqn. 3).

$$(3) \quad SO_3 \xrightarrow{H_2O} H_2SO_4$$

During the various operations carried out at elevated temperature, sulfur will be dispersed into the air in particulate form. This particulate sulfur can be deposited or be slowly oxidized.

Sulfur reacts with many organic compounds. Saturated hydrocarbons are dehydrogenated with formation of hydrogen sulfide (Eqn. 4). The, thus, generated olefins can add sulfur across the double bond forming organic sulfur derivatives, or can polymerize to hydrocarbons of higher molecular mass. Instead of olefin formation, sulfur may couple two hydrocarbon molecules (Eqn. 5) or yield an organic sulfide (Eqn. 6). Both of these reactions produce hydrogen sulfide.

$$(4) \quad RCH_2\text{-}CH_2R' \longrightarrow RCH = CHR' + H_2S$$

$$(5) \quad 2RH \xrightarrow{+1/8\ S_8} R\text{-}R + H_2S$$

$$(6) \quad 2RH \xrightarrow[+n/8\ S_8]{} R\text{-}(s)_{n-1}\ R + H_2S\ (n + 1,2,\ldots)$$

The reactions of sulfur with organic compounds are very complex and have not yet been elucidated in detail. The organic products formed in these reactions are expected to be non-volatile at the temperatures prevalent during preparation, placement and normal use of the sulfur-asphalt mixture. Hydrogen sulfide is the most important gaseous product of these reactions. The extremely poisonous gas, hydrogen sulfide, can be detected at concentrations as low as 0.02 ppm by its revolting odor but tends to dull the sense of smell at higher concentrations and during longer exposure. It is thermally very stable. Only 75% of a sample is decomposed at 3000°F (1649°C). In air, hydrogen sulfide under normal atmospheric conditions was estimated to be approximately four days [31]. Hydrogen sulfide and sulfur dioxide can then react to form elemental sulfur (Eqn. 8) which would appear in the air as particulate matter.

(7) $$H_2S \xrightarrow{\text{air}} H_2O + SO_2$$

(8) $$2H_2S + SO_2 \longrightarrow 3/8\ S_8 + 2H_2O$$

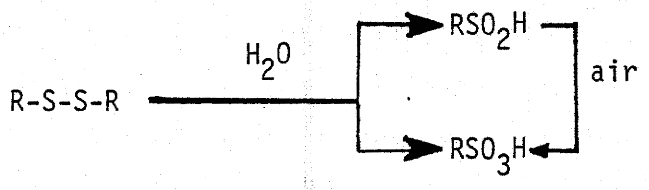
The reactions of sulfur with air or the hydrocarbons in the asphalt will produce large quantities of noxious gases at temperatures above 300°F (149°C). One can, therefore, expect to find sulfur dioxide, hydrogen sulfide and some sulfur trioxide and their reaction products with water in the air in the vicinity of locations where hot sulfur-asphalt mixes are handled, when the air is humid.

Under normal use, surface temperatures of sulfur-asphalt pavements are maintained below 300°F (149°C). Therefore, hydrogen sulfide and sulfur dioxide will very likely not be generated in amounts to exceed their Maximum Allowable Concentrations (MAC) [6, 7]. Slow oxidation of some of the sulfur will occur as described by (Eqn. 1).

An accident which causes a fire on such a pavement could locally raise the temperature of the mix high enough to generate hydrogen sulfide through reactions of sulfur with organic compounds (Eqn. 4, 5, 6). An additional part of the sulfur will burn to sulfur dioxide (Eqn. 1).

Sulfur-asphalt pavements are naturally exposed to the influence of atmospheric agents. The oxygen of the air will very slowly oxidize the sulfur to sulfur dioxide. This reaction is too slow to cause any pollution problems. It could also happen, that the organic sulfides in the mix are oxidized to sulfinic or sulfonic acids by oxygen (Eqn. 9).

(9)



$$\begin{tikzcd} & RSO_2H \arrow[d, "\text{air}"] \\ \text{R-S-S-R} \arrow[ur, "H_2O"] \arrow[r] & RSO_3H \end{tikzcd}$$

These acidic substances are more soluble in water than, for instance, the disulfides. They could be leached out by rain and enter surface and ground water streams. These compounds are related to snythetic surfactants, which are constituents of detergents, and should be biodegradable. Highly polar solvents such as water, deicing liquids, aqueous acids and alkalies are not expected to dissolve much more from the sulfur-asphalt pavement than from a pure asphalt mix. Depending on the strength of an alkaline solution part of the elemental sulfur can be converted to alkali polysulfides (Eqn. 10), which are soluble in an aqueous medium. In water

$$(10) \qquad \frac{n}{8}\ S_8 \xrightarrow[H_2O]{NaOH} Na_2S_n$$

containing dissolved oxygen these sulfides will be oxidized to sulfuric acid as the final product. Non-oxidizing acids, such as hydrochloric acid, do not dissolve sulfur. Oxidizing acids convert sulfur to sulfuric acid.

Sulfur will not be dissolved to an appreciable extent by engine oil, grease and gasoline. The organic sulfur compounds are more likely to be extracted from the pavement by these materials. Through the mechanical action of the atmospheric agents, sulfur particles can be torn loose from the pavement and enter the run-off.

1.1.4 Pollutants Encountered in Sulfur-Asphalt Mixes

General: Throughout the development of the sulfur-asphalt concept one of the major concerns of the industry has been the potential hazards created at the construction site due to the evolution of toxic gases (H_2S and SO_2) and particulate sulfur. Over the years Shell and Gulf have monitored these pollutants both in the laboratory as well as in conjunction with their full-scale field trials. As yet, none of their data has been reported in the open literature. However, Shell [1, 4] has stated that as long as the temperature of the mix is maintained below 300°F (149°C) the concentrations of H_2S and SO_2 produced are well below the maximum allowable concentrations as suggested by the American

Conference of Governmental Industrial Hygienists (ACGIH) [32]. Similar studies at TTI and the Bureau of Mines support this claim [6, 33]. For the sake of clarification the nature of the safety problem associated with these types of contaminants will now be discussed.

RELATIVE TOXICITY OF H_2S

Hydrogen Sulfide is known for its characteristic "rotten egg" odor. Although this odor is noticeable at concentrations as low as 0.02 ppm [32], odor is not a good indicator of concentration level. Hydrogen sulfide can have a paralyzing effect on the sense of smell [34]. Therefore, high and potentially fatal concentrations of H_2S can escape recognition.

The basis used for establishing the relative toxicity of emissions data generated during this project were the relationships between H_2S concentrations and human effects as specified by ACGIH [32, 35]. These relationships are shown below:

Toxicity of Hydrogen Sulfide [35]

Concentration, ppm	Effect
0.02	Odor threshold
0.10	Eye irritation
5-10	Suggested Maximum Allowable Concentration (MAC) for prolonged exposure
70-150	Slight symptoms after exposure of several hours
170-300	Maximum Concentration which can be inhaled for 1 hour
400-700	Dangerous after exposure for 1/2 to 1 hour
600	Fatal with 1/2 hour exposure

On the basis of these effects a MAC value of 5 ppm is normally specified as the upper threshold limit for continuous exposure to H_2S emissions in areas normally expected to be occupied by construction or plant personnel.

RELATIVE TOXICITY OF SO_2

Sulfur Dioxide (SO_2) is a colorless gas with a pungent odor which, unlike H_2S, gives ample warning of its presence. The principle health hazard from SO_2 comes from inhalation of excessive quantities above its MAC. The basis for establishing the relative toxicity of emissions data generated during construction should be the relationships between SO_2 concentrations and human effects as specified by the National Institute for Occupational Safety by Health and The Manufacturing Chemists Association [36] and shown in the following table.

Toxicity of Sulfur Dioxide [36]

Concentration (ppm)	
0.3 - 1	Detected by taste
1	Injurious to plant foliage
3	Noticeable odor
5	MAC (ACGIH)
6-12	Immediate irritation of nose and throat
20	Irritation to eyes
50-100	MAC for 30-60 min. exposures
400-500	Immediately dangerous to life

The present Federal standard for SO_2 in an 8-hour time weighted average of 5 ppm (see 29CFR, 1910,93 published in the Federal Register, Volume 37, p. 22139, October 18, 1972) [37]. This is the MAC specified as the upper threshold limit concentration for SO_2 emissions in areas normally expected to be occupied by construction of plant personnel.

PARTICULATE SULFUR OCCURRENCE AND TOXICITY

Vapor given off during mixing and dumping operations contain a certain amount of undissolved and unreacted sulfur. As the vapors come in contact with air and cool, the sulfur vapor crystallizes into small particles which are carried by the wind in a manner similar to dust and fine sands. Since there is no practical way to eliminate this pollutant, its effects on both environment and personnel need to be considered.

This section will be devoted to a discussion of the relative hazards associated with sulfur dust on construction personnel as specified by the Manufacturing Chemists Association [38]. Assessments of the environmental impact of this pollutant in sulfur pavement construction do not exist.

The principal problems associated with sulfur dust lie in its contact with eyes. Sulfur is virtually nontoxic and there is no evidence that systemic poisoning results from the inhalation of sulfur dust. However, sulfur is capable of irritating the inner surfaces of the eyelids. Sulfur dust may rarely irritate the skin. This problem is minimized by the requirement that goggles be worn in areas subject to this pollutant such as at the hot mix plant and in the vicinity of the paver.

The primary hazard in handling solid sulfur results from the fact that sulfur dust suspended in air may be ignited. This problem is almost always limited to enclosures and unventilated areas. Since this is not typical of the hot mix plant or the paving area this particular hazard is not a major concern.

To minimize possible irritation, unnecessary contact with skin and eyes should be avoided. Following the work period, sulfur dust should be removed with mild soap and water. For relief of eye irritation, eyes should be thoroughly flushed with large quantities of plain water or physiological saline. Inadequate amounts of water may actually increase eye irritation.

1.1.5 TTI's Experience with Evolved Gases from Sulfur-Asphalt Mixes in the Laboratory.

Throughout all of its sulfur-asphalt-sand (SAS) and sulfur extended asphalt (SEA) studies TTI continually monitored H_2S and SO_2

emissions produced during mix preparation and sample fabrication. At the outset virtually no SO_2 was detected in any of the operations and concern was directed primarily to monitoring H_2S. The results of this activity are reflected in two reports [30, 39]. The H_2S emissions which were encountered as a function of sulfur-asphalt (S/A) ratio in the mix are tabulated below:

Sulfur-Asphalt Ratio	H_2S Concentration, ppm Mean Range
2.25 (normal for Thermopave [1]	0.54 (0.20 - 1.80)
2.66	0.57 (0.54 - 0.60)
3.33	0.54 (0.54 - 0.60)
6.75	0.43 (0.30 - 0.50)
8.00	0.17 (0.15 - 0.20)
10.00	0.35 (0.08 - 1.0)

Both mean and ranges fell well within the suggested MAC levels for all S/A ratios tested. It should be mentioned that these data were taken 18 inches from the source (or surface of the mix) which was considered to be the normal working distance for laboratory personnel. All mixes were prepared at temperatures within the range suggested by Shell (i.e. 270°F to 300°F or 132°C to 149°C) the emissions above 300°F are shown in Figure 2.

The above data however do not reveal the true peak concentrations which occur upon initial mixing stages (i.e. when sulfur and asphalt are introduced into the mix). The peak loads detected produced more higher concentrations which dissipated in a matter of seconds. Such a comparison is shown in Figure 3 which compares the peak H_2S concentration during mixing (0 to 30 seconds after introduction of sulfur) with the concentration present at the end of a 3 minute compaction time for a mix with an S/A ratio of 2.5. Anticipated S/A ratio for sulfur-asphalt mixes range from 0.2 for SAE systems to 2.5 for sand-asphalt-sulfur mixes.

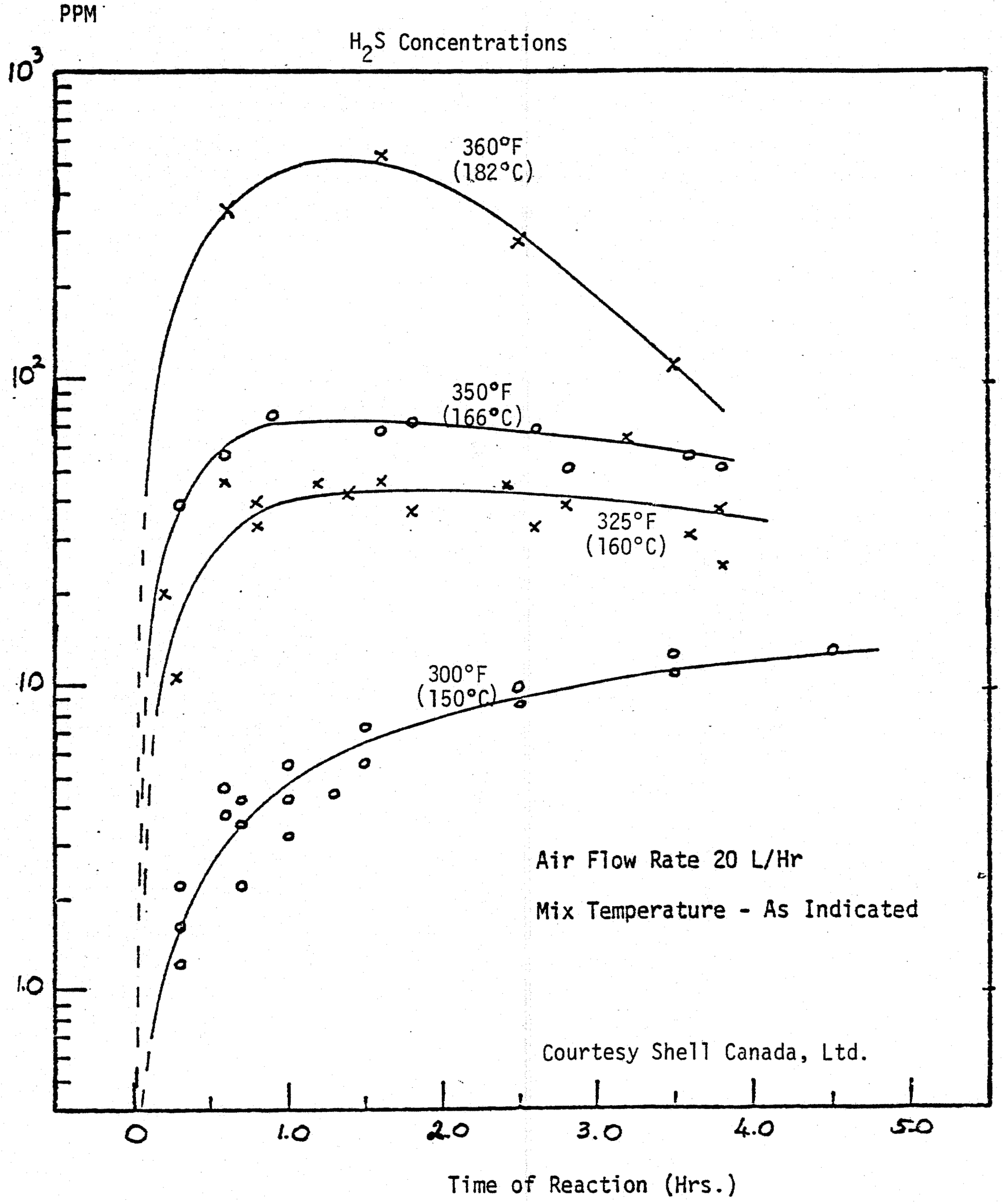


Figure 2. Effect of Temperature on Hydrogen Sulfide Concentration in SAS Mixtures as a Function of Reaction Time.

Figure 3 shows that the H_2S present within seconds after he contact of sulfur and asphalt took place during mixing was about 16.4 ppm. This concentration dipped to 0.4 ppm by the time the mix was ready for compaction about 3 minutes later. Although the figure does not indicate the total trace it was observed that H_2S concentrations were reduced to safe levels within 8-10 seconds after mixing was initiated.

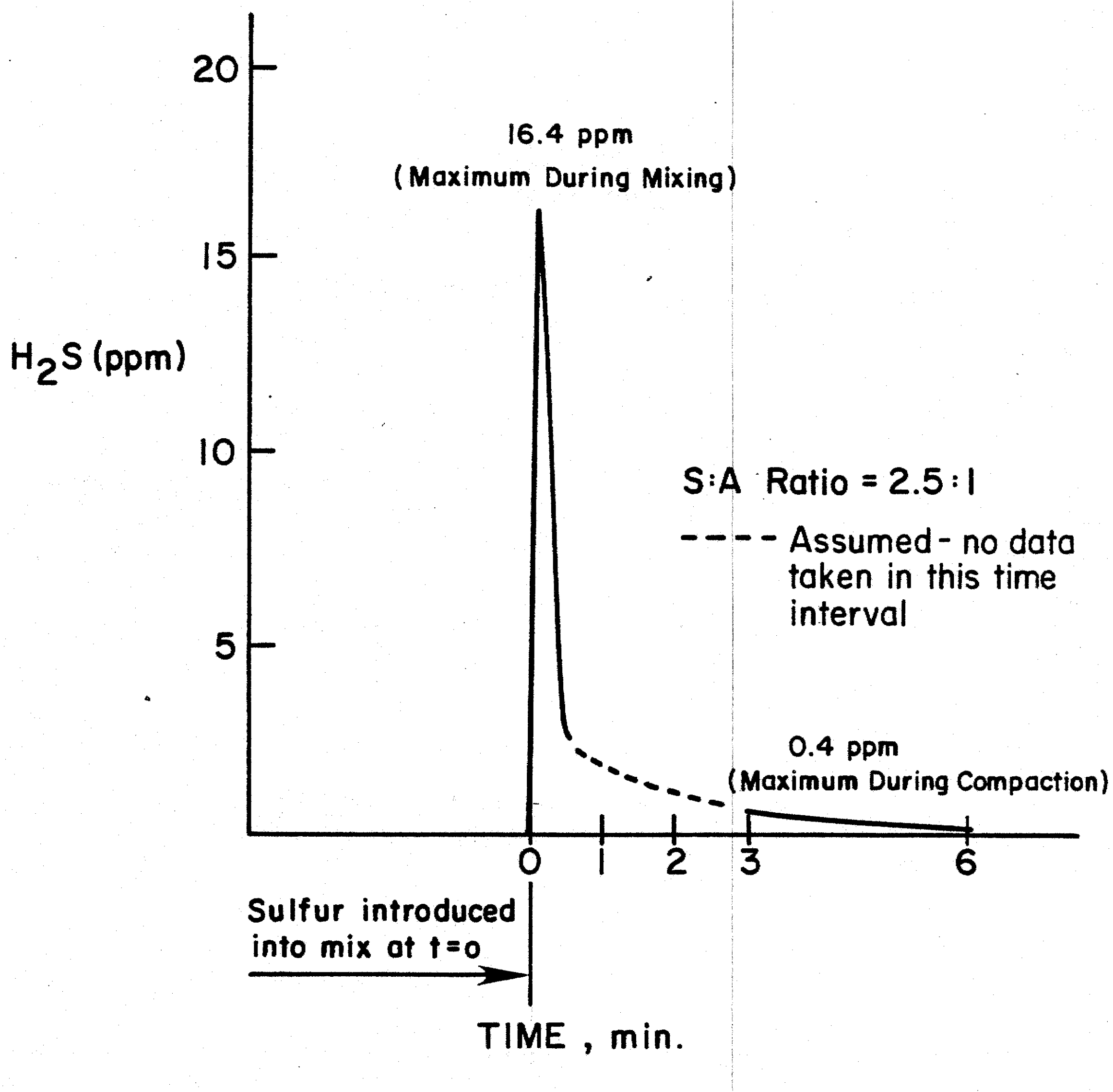


Figure 3. Comparison of H_2S Evolution During Mixing and Compaction.

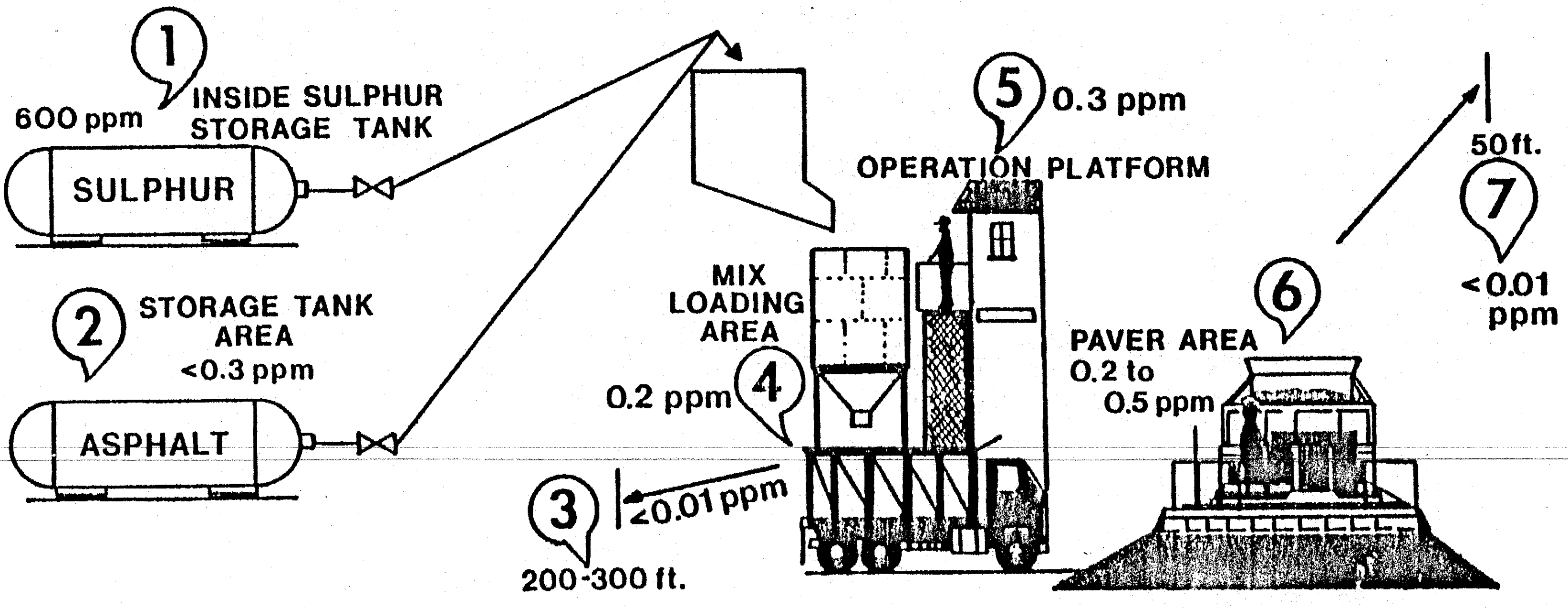
1.1.6 TTI's Experience with Evolved Gases from Sulfur-Asphalt Mixes-Field Trials.

Data on gaseous emissions were taken by TTI on both the Lufkin [13] and Kenedy County, Texas [7] sulfur-asphalt field trials. The Lufkin trials were only monitored for H_2S at virtually all important areas throughout the construction site. The results of this effort are indicated in Figure 4 which shows the H_2S concentrations at these locations. It should be noted that with the exception of the area inside the sulfur storage tank all H_2S concentrations were well below MAC values. Since this location is not considered to be a normal personnel area, safety considerations normally employed for sulfur handling would prevail [21].

Probably the most extensive emissions monitoring at a field test site was conducted by TTI along with personnel from the Bureau of Mines and the Texas Air Control Board (TACB) at the Kenedy County, Texas field trials. Details of that study are given in the construction report [7] for that project and will be summarized below.

The evolved gas measurements were taken during the construction period 5-7 April, 1977. TACB data were obtained using a mobile sampling van which moved about the various sampling sites. Specifically, measurements were taken at the following locations: Sulfur storage tank, hot-mix plant mixing chamber and the paver hopper and auger. Additional measurements were taken downwind of the plant and paver so as to establish dissipation factors.

Except for downwind samplings, most of the emissions readings generated by TACB were considered to be "source" type data; that is measurements were taken directly over the mixture. Samples were collected with a 5-ft. (1.5m) probe of 3/8 in. (9.5 mm) O.D. stainless steel tubing. Gases were sucked back to the analyzer through a 1/4 in. (6.4 mm) polyethylene tube by a Metal Bellows Company, Model MB-41 pump. Samples were collected by placing the probe tip at distances



1 ft. = 0.31 m

Figure 4. Anticipated H_2S Levels During Mixing and Paving

which ranged from 1 to 12 inches (25.4 mm to 305 mm) from the surface of the material from which the gases were being evolved. These distances are much less than that normally occupied by personnel which normally range from 2 to 6 ft. (0.6 to 1.8 m). Hence the designation "source data" were assigned to these samplings. As a backup to the source data collected by TACB, both TTI and the Bureau of Mines samplings were obtained at locations more representative of those which might be expected to be occupied by personnel.

One such area was on the platform of the hot-mix plant where the various mix ingredients were introduced into the pug mill. Continous samplings over a 24-hour period were taken in the vicinity of the manually operated feed controls at a height equal to nose level of the operator. Additional 24-hour continous samplings were taken at a point under the pug mill and just over the dump bodies of the trucks. Both of these points were monitored using a Houston-Atlas Sampler with a continuous read-out. This unit was furnished by the Bureau of Mines Metallurgy Research Laboratory of Boulder City, Nevada.

TTI personnel took samplings for both H_2S and SO_2 using two types of portable sensing instruments. A Metronics Model 721 "Rotorod" Gas Sampler [29] which is designed for monitoring only H_2S emissions was used to collect data in the vicinity of the plant, within the quality control testing laboratory, inside the cabs of hauling trucks, at the paver operator's seat, alonside the paver, at the paver's hopper and auger and in the vicinity of the sulfur storage tanks.

The other portable sampler employed was a Drager Tube with a manually operated bellows. Appropriate calibrated tubes for monitoring both H_2S and SO_2 were used with this device.

Samplings were taken at essentially the same locations monitored by the Metronics Rotorod Sampler. Drager tube measurements of H_2S concentrations thus provided a back up to those taken with the Rotorod Sampler.

KENEDY COUNTY TEST RESULTS

The results of the measurements taken of H_2S concentrations at various locations of the construction site and plant are given in Tables 1 to 3.

Table 1 includes data taken at and in the vicinity of the hot mix plant and sulfur storage area. Table 2 contains emissions monitored in the vicinity of the paving operation. Table 3 includes all other areas monitored. Data are presented in a manner to reflect locations, sampling agency (TACB, TTI or both), sampling equipment, average concentration and supporting remarks.

As has been reported, as long as the temperature of sulfur-asphalt systems were maintained below a maximum of 300°F (149°C), H_2S emissions were found to be well below suggested MAC values. Except for several occasions when screed temperature control was lost, H_2S concentrations as measured in locations normally frequented by construction personnel, were found to be significantly less than 5 ppm. The fact that no complaints were registered during the entire construction period supports this conclusion. In some cases "source type" emissions; that is, samplings taken directly over the mix material, appeared to be excessively high. However, in an open-air environment these concentrations are rapidly reduced with distance.

The highest concentrations encountered, as was the case at Lufkin, were at or near the loading port of the sulfur storage tank and inside the pug mill. Since these are not considered to be personnel areas the safety hazards are considered to be minimal".

All measurements of SO_2 concentrations were monitored by TTI using the Drager Tube. The data given below show the ranges of SO_2 concentrations measured at various locations at the paving site.

Table 1. H_2S Emissions at and in the Vicinity of the Hot Mix Plant.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - personnel area
<u>Sulfur Storage Tank Area</u>				
a) Tank Inlet Port	TACB	Telematic	2939	NPA
b) 5 ft. from Tank Inlet Port	TACB	Telematic	23	NPA
c) On the ground at the base of the sulfur storage tank	TTI	Totorod	0.9	PA (moderate)
d) Ground level between sulfur tank and Hot Mix Plant Kiln	TACB	Telematic	0.02	PA (moderate to dense)
<u>Hot Mix Plant Area</u>				
a) Operator Platform	TACB	Telematic	0.007	PA (1-2 people)
	BOM	Houston - Atlas	0.5 to 2.0	PA (1-2 people)
	TTI	Rotorod	Trace	PA (1-2 people)
	TTI	Drager Tube	Trace	PA (1-2 people)
b) Base of Platform	TTI	Rotorod	Trace	PA (light)
Stairwell	TTI	Drager Tube	Trace	PA (light)
c) At Pugmill Discharge and Over Dump Body	BOM	Houston-Atlas	0.5 to 0.6	NPA
d) 125 ft. downwind of Hot Mix Plant	TACB	Telematic	0.01	PA (light)
	TTI	Rotorod	Trace	PA (light)

1 ft. = 0.31 m

Table 2. H_2S Emissions at and in the Vicinity of the Paver.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks NPA - non personnel area PA - personnel area
Paver				
a) Floor at Paver Operator's Feet	TACB	Telematic	1.4	PA (1 person)
b) In Paver Operator's Chair	TTI	Rotorod	Trace	PA (1 person)
	TTI	Drager Tube	Trace	PA (1 person)
c) Paver Hopper	TACB	Telematic	4.3	NPA
	BOM/TTI	Drager Tube	2-5	NPA
d) Alongside Paver (at Auger) Downwind	BOM/TTI	Drager Tube	0-20*	PA (1-2 people)
e) Over Paver Auger	BOM/TTI	Drager Tube	20-80*	NPA
Paver Vicinity				
a) 300 ft. Upwind	TACB	Telematic	0	PA (light)
b) 25 ft. Downwind	BOM/TTI	Drager Tube	0	PA (light)
c) 100 ft. Downwind	TACB	Telematic	0.2	PA (light)
d) 200 ft. Downwind	TACB	Telematic	0	NPA
Over Pavement Behind Paver				
a) 0.5 ft. over surface	TACB	Telematic	1.3	NPA
b) 2 ft. over surface	BOM/TTI	Drager Tube	Trace	NPA

*Highest concentrations were encountered during a period when temperature control of the screed was lost causing mix temperature to exceed 320°F. (160°C). When temperature was reduced below 300°F (149°C) concentrations were reduced to near minimum values.

1 ft. = 0.31 m

Table 3. H_2S Emissions At Miscellaneous Locations.

Location	Sampling Agency	Sampling Equipment	Average Concentration (ppm)	Remarks
Dump Trucks				
a) Inside Cab at Hot Mix Plant	TTI	Rotorod	0.1	PA (1 person)
b) Inside Cab at Paver During Dump	TTI	Rotorod	0	PA (1 person)
c) Over Inlet to Dump Body	TTI	Rotorod	0.2	NPA
d. Inside Dump Body During Cleaning Operation	TTI	Rotorod	0.3	PA (1-2 persons)
Hot Mix Plant Quality Central Test Laboratory	TTI	Rotorod	Trace	PA (2-3 persons)
Hot Mix Plant Parking Area	TTI	Rotorod	0	PA (light)
At Sulfur Truck During Transfer to Storage Tank	TTI	Rotorod	0.4	PA (1-2 persons)

Location	Range (ppm)
Above paving hopper	0 - 0.5
Alongside paver (downwind)	0.5 - 20
Behind paver	0
Paver operator seat	0
Hot mix plant platform	Trace
Inside truck cab	Trace
Vicinity of sulfur storage tank	3 - 12
Directly over paved surface	0

As indicated, the values varied considerably with some concentration levels exceeding the MAC value recommended by ACGIH. These values were obtained primarily in areas of minimal worker exposure such as the vicinity of the sulfur storage tank and very close to the material in the paver. The latter were attributed to the deliberate overheating of the paver screed, a temporary event, which occurred near the end of construction. After these readings were taken the screed temperature was reduced and the concentrations were subsequently reduced to the lower values indicated above.

The paver screed without suitable temperature controls, would appear to be the main source of potentially high H_2S and SO_2 emissions. At typical operator and workmen locations on the paver and at the hot mix plant platform gas toxicity was negligible. As in the case with H_2S, gas evolution stayed well below established MAC limits when mix and paving temperatures were maintained under 300°F (149°C). Evolved gas analyses were carried out at a number of other field trials including Lufkin, Texas (1975), Bryan, Texas (1978) [14], Boulder City, Nevada (1977) and Tucson, Arizona (1979). In general, the emissions detected were well within the MAC values and consistent with the anticipated concentrations shown in Figure 4.

Only a limited amount of particulate sulfur measurements have been taken to date. The Bryan, Texas project [14], utilized a number of "Hi-Vol" dust collection units (Figure 5) stationed at various locations in the vicinity of the hot mix plant and at the paving site. Air was

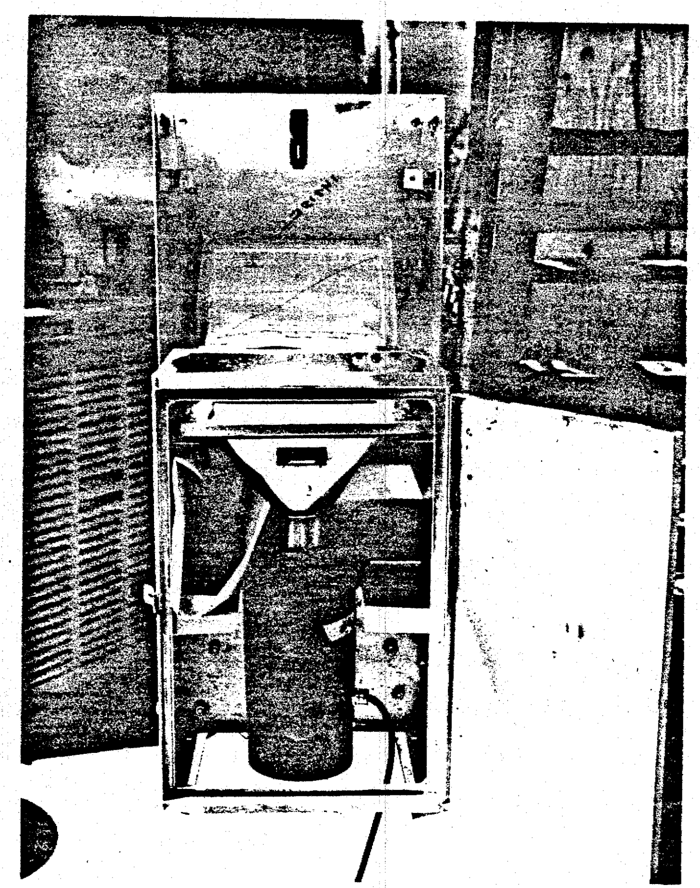


Figure 5. Hi Vol Dust Collector Utilized for Measuring Particulate Sulfur at the Plant and Job Site.

drawn into a covered housing and through a filter by means of a high flow-rate blower at a flow rate of 40 to 60 ft^3/min (1.13 to 1.17 m^3/min) which allowed suspended particles having diameters less than 10 m to pass to the filter surface. The mass concentration of the particulates in the ambient air (g/m^3) was computed by measuring the mass of collected particulates and the volume of air sampled. The total particulate matter collected by the four Hi-Vol units were analyzed in accordance with ASTM E30-40, the results of which are shown in Table 4. The amount of total particulate sulfur present was so minute that it was not deemed to be a hazard even regarding eye irritation.

1.1.7 Summary

The relative toxicity of three forms of sulfur pollutants (H_2S, SO_2 and sulfur dust) were discussed. As long as the mix temperature is not permitted to exceed 300°F (149°C), concentrations of the two gaseous pollutants can be expected to remain below recommended allowable threshold limits. This condition indicates the need to provide positive temperature controls at both the hot mix plant and the paver.

Although only limited amounts of data on sulfur dust generated during construction have been obtained to date, experience dictates that the only major hazard to personnel lies in irritation to eyes. Safety goggles are recommended to offset this problem. No on-the-job observations taken as yet would indicate that sulfur dust is present in sufficient quantities to create a health hazard. It has been recommended that additional data on sulfur dust be generated on any future sulfur-asphalt field trials.

The location where highest concentrations of H_2S and SO_2 can be expected at a job site will be in the sulfur storage area more specifically near the loading ports of the storage tank which is not considered a personnel area. Furthermore, the concentrations of the pollutants decrease rapidly with distance thus eliminating this area as a potential safety hazard to plant workmen. Normally

TABLE 4. Particulate Sulfur Measurements

Location	mg Total Sediment	mg Total Sulfur	Sediment Flux $mg/m^3/day$	Sulfur* Flux $mg/m^3/day$
Test Site, 35 ft Easterly from Engineer Station 57+10	120.07	0.654	205.73	1.12
Test Site, 35 ft Easterly from Engineer Station 58+20	139.5	0.630	249.98	1.13
Hot-Mix Plant, on Ground Between Binder Plant (Mill) and Pug-mill	1275.96	1.634	3198.40	4.10
same	1008.47	0.595	498.1	2.94
Hot-Mix Plant, Downwind Northerly	199.68	0.011	1126.2	0.06

* Not particulate Sulfur Exclusively - Test Results to follow (8-11-78)

Note: Measurements of Sediment Flux and Sulfur Flux are based 8-hour day.

The total matter collected by the High Volume units were analyzed by following ASTM Standard E 30-47.

accepted safety practices [24-26] should be employed during transfer of hot sulfur from delivery trucks to the storage tanks.

2 OVERALL PROGRAM PURPOSE, SCOPE, AND OBJECTIVES

2.1 Purpose

The purpose of this investigation was to evaluate the environmental and safety hazards along with the development of safety guidelines associated with the use of sulfur in highway pavements. This was accomplished by virtue of a series of laboratory and simulated field tests in which the safety and environmental aspects of materials storage and handling, formulation, construction, operation and maintenance of highway pavements containing sulfur were evaluated. The structuring of these tests and the evaluation of the results were complemented by the preparation of a field evaluation plan in which the sources, relative toxicity, safety and methods of monitoring and analyzing pollutants were identified. An annotated bibliography specifically oriented to the safety and environmental effects associated with sulfur-modified paving materials preparation and construction was also prepared.

2.2 Scope and Objectives

The long range objectives of the study were to evaluate the environmental and safety hazards and define some safety guidelines for the use of sulfur in highway pavements. Consideration was given to the possible evaluation and identification of toxic and obnosious fumes, dusts and runoffs which might be produced during formulation, storage, construction and maintenance of sulfur modified paving materials. This scope was extended to consider effects on humans, animals, soils, highway structural materials, ground waters and vegetation. The investigation was carried out in four tasks:

Task A - Laboratory Identification and Evaluation of Hazardous Materials and Conditions

Task B - Human Safety and Environmental Aspects

Task C - Field Evaluation Plan
Task D - Annotated Bibliography

and the final report was prepared in the following three volumes to provide a basis for selective and more cost effective distribution.

Volume I - Evaluation of Environmental and Safety Hazards
Volume II - Field Evaluation Plan
Volume III - Annotated Bibliography

Volume I contains primarily the results of the effort in Tasks A and B, the conclusion and recommendations generated in Task C and a discussion of the scope of Task D. Volume II provides a more detailed treatment of the field evaluation plan and Volume III the individually synopsized list of references. The latter have been codified, cross referenced and set up to permit easy updating.

3 TECHNICAL PROGRAM

3.1 Task A - Laboratory Identification and Evaluation of Hazardous Materials and Conditions

This task studied a number of different mix designs representative of typical sulfur-modified paving materials. Both sulfur-asphalt systems and sulfur concrete were considered. Mix designs were not selected on the basis of any structural capability and, as such, would not necessarily be considered optimum. They were chosen so as to represent a range of sulfur contents, and aggregate gradations, additives and specialty concepts (e.g., recycled mixes). The work plan for Task A is given in Figure 6.

Emissions, contaminants, environmental impact and possible anomolous behavior were examined under four conditions: (a) mix preparation, (b) weathering, (c) simulated fire and (d) chemical spills and surface treatments such as salt and deicers. Mix preparation was conducted over three temperatures, two within the normal working range for sulfur paving mixtures and one at an abnormally high temperature as might be encountered when temperature control is lost. Other process variables include humidity and oxygen levels.

Weathering studies were designed to look at the effects of long term exposure to the elements, run-off during rainfall conditons, of pavement materials and leachates produced by exposure to high surface temperatures, ultra-violet (actinic) light, freeze-thaw cycling and traffic wear. Biological activity and concomitant weathering were also considered.

The potential of the sulfur systems for catching fire, sustaining a burn and creating pollutants during combustion were also assessed. Finally, the resistance to attack by surface treatment chemicals such as brines and deicers were studied relative to safety and environmental impact.

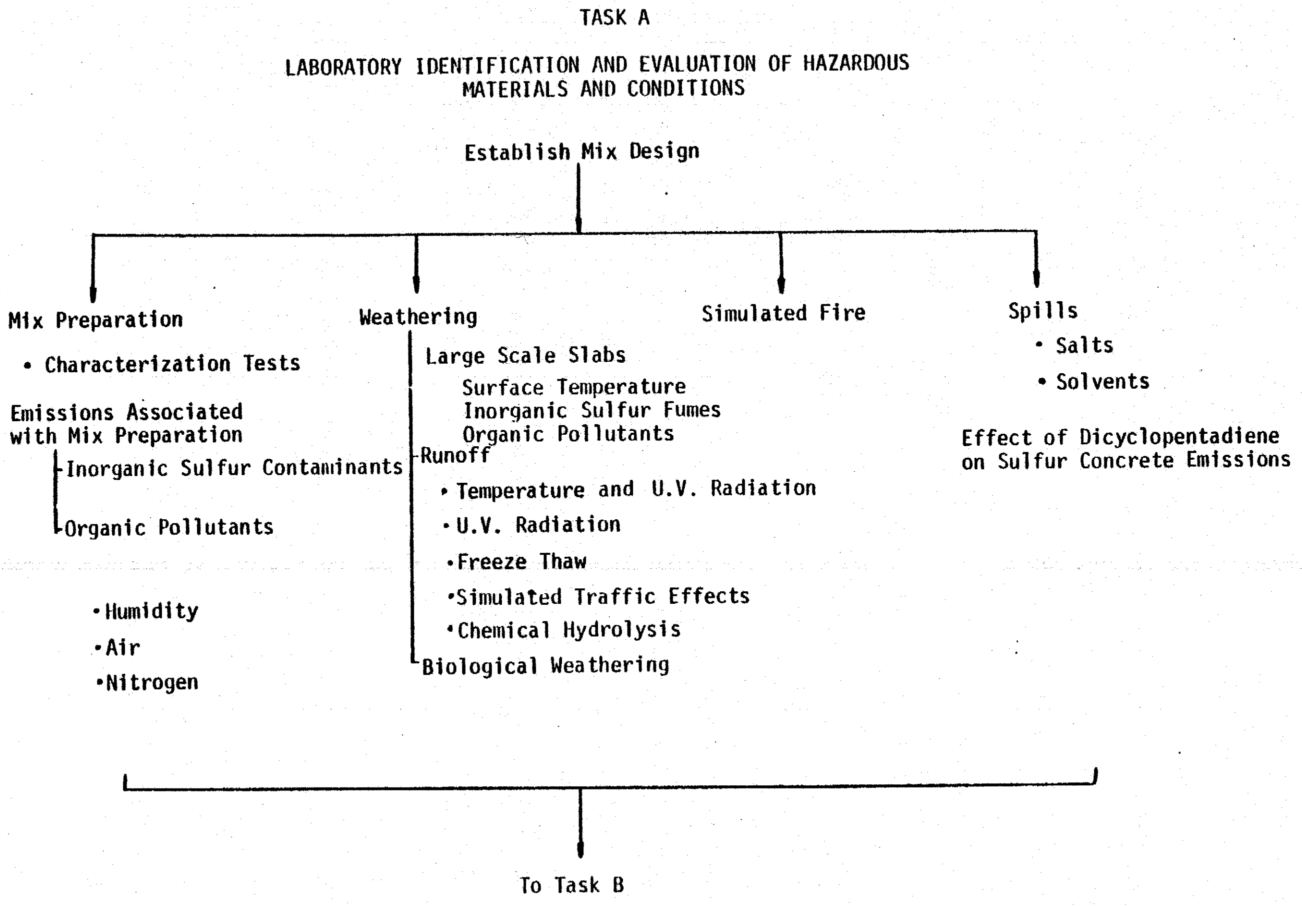


Figure 6. Task A Work Plan.

3.1.1 Mix Design Preparation.

The evaluation was conducted on three different types of sulfur-asphalt mixes; (a) aggregate-asphalt-sulfur (A-A-S), (b) sulfur extended asphalt (SEA) and sulfur recycled. Included in the SEA series were mixes prepared with both dense and open graded aggregate systems. For comparison purposes a conventional dense graded asphaltic concrete system was used as a control.

During the mix preparation phases difficulty was experienced with the AAS - open graded system. AAS mixes possess characteristically high sulfur contents (i.e. Sulfur/asphalt ratios ∿ 2 to 1). Because of the permeability of the open graded aggregates, seepage of the low-viscosity, liquid sulfur resulted in poor homogeniety in the samples prepared. The problem persisted until the sulfur content was reduced below 30 weight percent of binder. This approached the sulfur content of the direct blended SEA open graded mix. Therefore a "practical" AAS, open graded mix was considered to be unachievable.

In addition to the sulfur-asphalt systems, two sulfur concrete mixes were prepared. One mix was a sulfur-aggregate system with no additives while the other contained Dicyclopendadiene (DCPD) at 5 percent by weight of sulfur. The aggregate was a 50/50 rounded gravel/concrete sand blend.

The selection of the materials and the resulting mix designs for the preparation of laboratory samples which were used throughout the program are shown in Tables 5, through 8. Table 5 is a list of the selected mix materials and sources. Tables 6 and 8 contain the mix designs for seven sulfur-asphalt and four sulfur concrete systems, respectively. Table 7 contains the notations for Sulfur-Asphalt systems.

3.1.1.1 Characterization Tests.

The results of the characterization tests (see Table 9) conducted

Table 5. Selected Concrete Materials.

Asphalt Cement

Designation: AC-10

Source: American Petrofina
Mt. Pleasant, Texas

Elemental Sulfur

Designation: Sulfur

Source: Stauffer Chemical Co.
Specialty Chemical Division
Westport, Connecticut

Aggregates

Designation: Crushed Limestone

Source: Texas Crushed Stone
Burnett, Texas

Designation: Rounded Gravel

Source: Gifford-Hill
Bryan Pit

Designation: Concrete Sand

Source: Gifford-Hill
Bryan Pit

Designation: Beach Sand

Source: TAMU Stockpile -
obtained from Padre Island
Corpus Christi, Texas

Table 6. Selected Mix Designs and Materials for Laboratory Samples of Asphaltic Concretes.

Mix Number	Mixing*** System	Binder Proportions	Binder Content	AGGREGATE	
				Material	Gradation
1	Aggregate -Asphalt (AAS)	25% Sulfur 75% Asphalt	6.9 w/o	Crushed Limestone	Dense*
3		70% Sulfur 30% Asphalt	19.5 w/o	Beach Sand	Uniform
4		1.25% Sulfur 0% Asphalt	1.25 w/o	Nellis Runway Recycled Material	Dense
5		1.25% Sulfur 1.0% Asphalt	2.25%		
2	Aggregate -Emulsion (AE)	25% Sulfur 75% Asphalt	6.9% w/o	Crushed Limestone	Dense
7		20% Sulfur 80% Asphalt	≈4 w/o		Open**
6	Asphaltic Concrete (AC) (Control)	0% Sulfur 100% Asphalt	4.5%	Crushed Limestone	Dense

*Asphalt Institute Gradation IVb.

**Texas Highway Department Grade 4.

***Definitions of notations and symbols used in identifying mix types and designs are given in Table 7, page 35.

Table 7. Notations for Sulfur-Asphalt Systems.

Notation (Alphabetically)	Definition
AAS	Aggregate - Asphalt - Sulphur Mix System
AAS (SAND	AAS System with Sand as the Aggregate
AC	Asphaltic Concrete
ARM	Asphalt Recycled Mix
SEA	Sulfur Extended Asphalt (Asphalt and sulfur combined as an emulsion then added to aggregate)
SRM	Sulfur Recycled Mix
V/o	VOLUME Percent of Mix
v/o	VOLUME Percent of Binder
W/o	WEIGHT Percent of Mix
w/o	WEIGHT Percent of Binder

Table 8. Selected Mix Designs and Materials for Laboratory Samples of Sulfur Concretes.

Mix Number	Sulfur Content	Additive* Content	AGGREGATE	
			Material	Proportion
100	24%	0%	Rounded Gravel	50%
			Concrete Sand	50%
101	20%	by 5% Weight of Sulfur	Rounded Gravel	50%
			Concrete Sand	50%

*The Additive will be Dicyclopentadiene (DCPD).

Table 9. Properties of the Laboratory Sulfur-Asphalt Mix Design*.

Description of Mix	Resilient Modulus @ 68°F (M_r. x10^{-6} psi)	Marshall Stability @ 140°F (lbs.)	Marshall Flow @ 140°F (0.01 in.)	Compacted Unit Weight lbs/cu.ft. (kg/M^3)	Air Voids (Percent Volume)
Mix 1 AAS 1.8 W/o S 5.1 W/o A	0.68	1970	9	152 (2430)	2.0
Mix 2 SEA 25 w/o S 75 w/o A	0.62	1977	9	151 (2420)	2.4
Mix 3 AAS (SAND) 13.5 W/o S 6.0 W/o A	0.40	3143	8	124 (1980)	8.6
Mix 4 SRM 1.25 w/o S 0.0 w/o A	2.90	6110	13.5	150 (2460)	2.0
Mix 5 SRM 1.25 w/o S 1.00 w/o A	1.60	3007	1.9	151 (2420)	1.6
Mix 6 AC 4.3 W/o A 0.0 W/o S	0.38	1790	8.5	146 (2340)	5.6

1 psi = 6.89 kPa
1 lbf = 4.45 N
1 in = 25.4 mm
1°F = 1.8 (°C) + 32

* These values are the average of tests made in triplicate.

on laboratory samples of sulfur extended asphalt were generated using the tests listed below:

1) Resilient Modulus at 68°F [40]
2) Marshall Stability and Flow (ASTM D 1559)
3) Compacted Unit Weight (ASTM D 1188)
4) Air Voids (ASTM D 1188)

A number of batches of sulfur concrete was prepared in accordance with the two mix designs given in Table 8 (i.e., one of sulfur concrete without additives, the other a sulfur concrete modified with 5 percent DCPD by weight of sulfur). The mixes were cast into 2-inch diameter by 4-inch long cylinders for compression and splitting tensile tests. Table 10 lists the results of these tests.

Table 10. Maximum Compressive and Tensile Stresses - Test Results for Sulfur Concrete.

Sample	Maximum Stress, psi Compressive	Splitting Tensile
SD-1	4490	1010
SD-2	5160	1160
SD-3	5190	1180
Average	4950	1085
S-1	2480	670
S-2	2610	860
S-3	2900	760
Average	2660	760

SD - Refers to sulfur concrete with DCPD (Mix Design 101 - Table 8).

S - Refers to sulfur concrete without plasticizer (Mix Design 100 - Table 8, page 35

The compression test was run in accordance with ASTM-C69 and the splitting tensile test was in accordance with ASTM-C496-71. It can be seen that sulfur concrete with DCPD had higher compressive and tensile strengths than did the unmodified mixtures. All samples were at least 14 days old when tested. As a matter of note the DCPD modified samples had normal failure characteristics whereas the unmodified specimens experienced localized failure indicative of poor aggregate-sulfur bonding.

3.1.2 Emissions Associated with Mix Preparation

Emissions generated during mix preparation were investigated as functions of mix design, temperature, and atmosphere (i.e., humidity, nitrogen). The primary objective of the experiment was to determine the concentrations, if any, of H_2S, SO_2, SO_3 elemental sulfur and organics released due directly to the incorporation of sulfur into formulation of sulfur-modified paving materials under the above environmental conditions.

The mix designs evaluated in this subtask are given in Table 11 and will be designated as MD-1 through MD-9. The specific environments selected for this evaluation are given below.

Temperature	(3),	°F	250	300	350
		(°C)	(121)	(149)	(176)
			Dry	Moist	Dry
Atmohspheres	(3),	%	5	95	N_2

3.1.2.1 Inorganic Sulfur Contaminants

The apparatus used to measure H_2S and SO_2 emissions is shown in Figure 7. Materials used in the study were prepared in bulk by proportioning the mix ingredients into a vat heated to 250°F (121°C) and mixing for 30 seconds. This was done to insure representative subsamples to differentiate between mix designs for the various

Table 11. Mix Designs Used in Task A Laboratory Evaluations.

Number	System	Weight Percent, w/o*		Binder Content, w/o	Aggregate Material	Gradation
		Sulfur	Asphalt			
MD-1	AAS	1.8	5.1	6.9 (Asphalt)	Crushed Limestone	Dense
MD-2	SEA	25	75	6.9	Crushed Limestone	Dense
MD-3	AAS	70	30	19.5 (Asphalt)	Beach Sand	Uniform
MD-4	Recycled	1.25	0	1.25	Nellis AFB Runway	Dense
MD-5	Recycled	1.25	1.0	2.25	Nellis AFB Runway	Dense
MD-6	A/C	0	100	4.5	Crushed Limestone	Dense
MD-7	SEA	20	80	4.0	Crushed Limestone	Open
MD-8	Sulfur Concrete	24	0	24	Gravel/Sand	Dense
MD-9	Sulfur Concrete w/DCPD**	21	0	21	Gravel/Sand	Dense

*In SEA systems sulfur and asphalt proportions are given as weight percent of binder. All others are given as percent of total mix.

**Dicyclopentadiene (DCPD) was added at 5 percent by weight of sulfur.

parameters tested. Following the initial mix the materials were cooled immediately and ground to pass a 1 mm mesh sieve. Sample manipulation in this manner was necessary to reduce the variability within mix designs to a manageable level.

A 3 g sample of a given mix design was placed in a flask and heated at a rate of 7°F (3.9°C) per minute. Air was drawn over the sample at a measured rate of 1 to 3 liters per minute and subsequently mixed with a measured volume of dilution air. Sampling times were determined by emission levels. This was done so not to induce another variable associated with the amount of sulfur initially in the sample. For example, measured emissions would be erroneously diminished if air was continually drawn through the apparatus once sulfur losses were materially reduced. Sampling time for the 250°F (121°C) measurements averaged about 20 minutes. The interval was reduced to approximately 10 minutes for the 350°F (177°C) measurements. A suitable fraction of the air mixture was drawn through and monitored by H_2S and SO_2 meters (Interscan models 1176 and 1248), respectively.

Concentrations of H_2S and SO_2 were monitored at equilibrium formulation temperatures of 300°F (149°C) and 250°F (121°C) and 350°F (177°C). In addition, the impact of oxygen and relative humidity on gaseous emissions were evaluated for the high sulfur-asphalt blend (MD-3) relative to the above formulation temperatures.

Relative humidities of 5% and 95% for nitrogen and air drawn through the reaction vessel were achieved by either driving the sweep gas with anhydrous $CaSO_4$, or saturating with water vapor. Vapor flux values (See section 3.1.3.3 for definition of flux) were calculated by converting concentration expressed in µl/liter to total mg H_2S or SO_2 evolved, then dividing this number by sample weight in K_g and the time interval in minutes.

Particulates generated were trapped onto a pre-weighed 0.1 µm filter disc. The stainless steel filter housing was heated at a slightly higher temperature than the reaction vessel to circumvent the problem of clogging the filter with condensed vapors, which would hamper the ability to maintain the calibrated flow rates. The reaction vessel was cooled prior to removal of the heated filter in order to reduce the potential for condensation error. The filter was dismantled while still hot and the filter disc removed to a vacuum dessicator for cooling prior to gravimetric analysis.

The SO_3 emissions were quantified on separate subsamples by selective absorption into 80% isopropanol, followed by titrametric analysis [41] as sulfate expressed as elemental sulfur (SO_4-S). Isopropanol was prepared by diluting 80 ml of 100% peroxide free isopropanol with 20 ml deionized water. A 25 ml aliquote of the isopropanol was placed in a 100 ml pyrex bubbler. The bubbler was immersed in an ice bath and placed in line with the sweep gas downstream of the mixing chamber depicted in Figure 7.

In constrast to the closed or controlled environment provided by the test apparatus shown in Figure 7, another series of emissions measurements were made for mixes prepared in an open laboratory environment. Gases were monitored using the H_2S and SO_2 Interscan meters. To better simulate normal operating conditions the above measurements were made at approximately 18 inches (46 cm) from the surface of the mix.

3.1.2.2 Organic Pollutants

The apparatus used to collect organic emissions is shown in Figure 8. Collection of organic emissions entailed heating the sample to a desired temperature, followed by a sweep gas purge into refrigerated solvent (benzene, hexane or petroleum ether) traps. Sweep gas was drawn over the sample at 2 liters per minute for 15 minutes.

Contents of a 2-trap series were combined, passed through anhydrous Na_2SO_4, and reduced in volume by vacuum distillation for

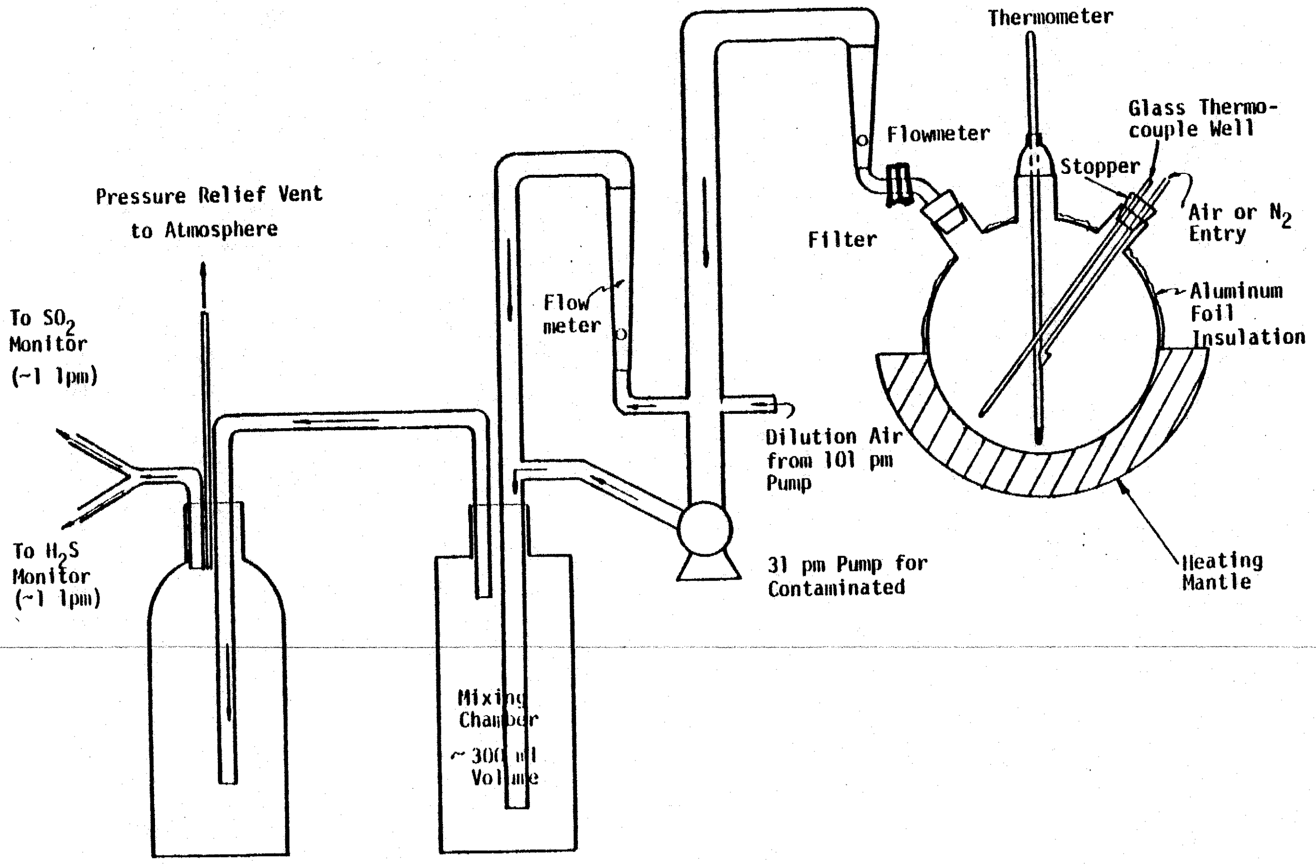


Figure 7. Apparatus for Collecting Inorganic Sulfur Contaminants - controlled environment.

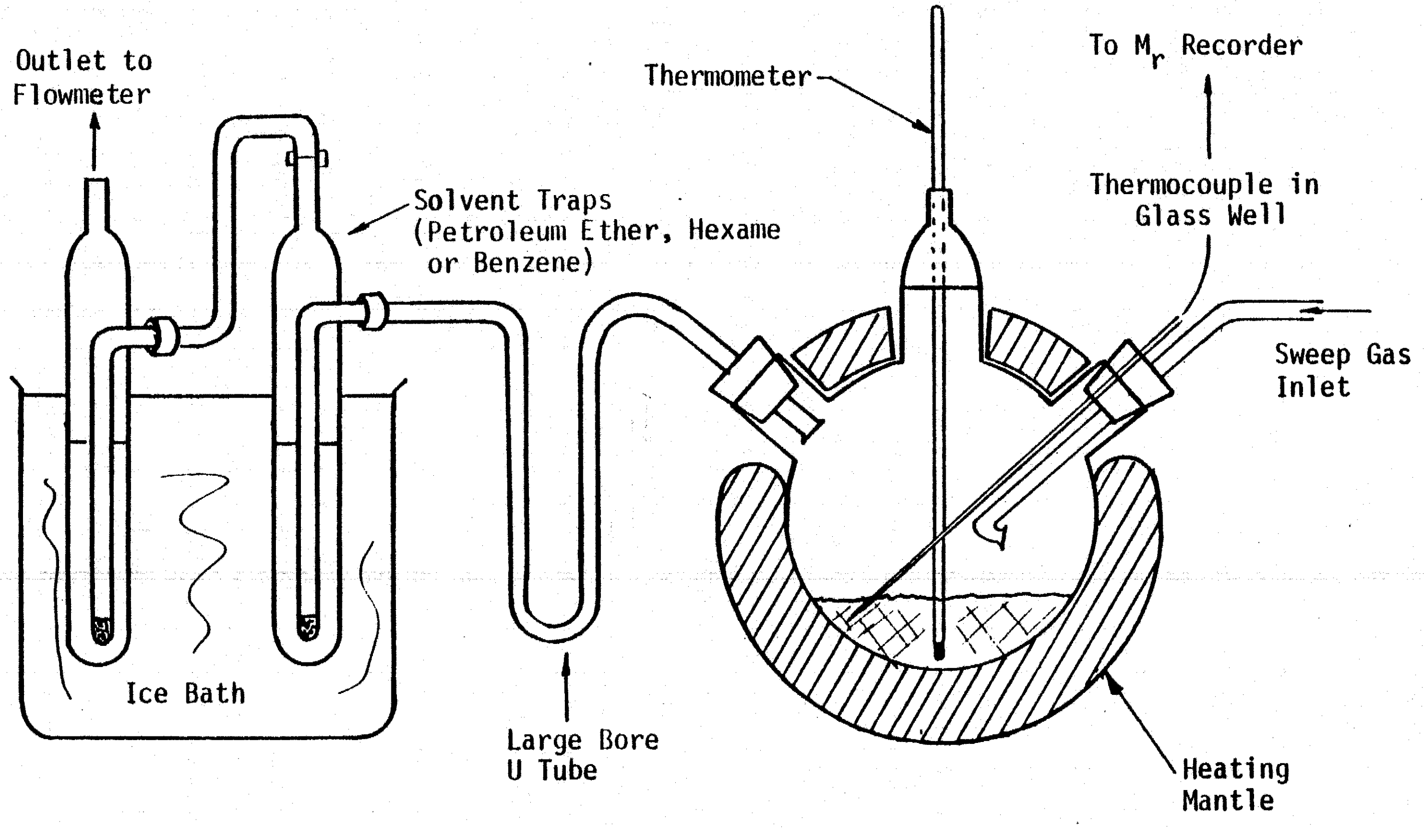


Figure 8. Apparatus Used to Collect Organic Emissions

subsequent gas chromatographic (GC) analyses.

Mercaptans were collected separately by a selective trapping technique [42, 43]. A bubbler containing 25 ml of 5% $HgCl_2$ solution with 0.3 ml of 5% NaOH added to adjust the pH was placed in line with the sweep gas in lieu of the refrigerated solvent traps. Two glass fiber filters impregnated with $KHCO_3$ and $ZnCL_2 + H_3BO_3$ immediately preceeded the bubbler to scrub SO_2 and H_2S gases, respectively. The SO_2 scrubber was prepared by saturating glass fibers, packed in a 0.1 in. (0.3 cm) I.D. by 2 in. (5 cm) glass tube, with a 5% $KHCO_3$ solution. A similar scrubber was constructed by saturating the glass fiber pack with a saturated $ZnCl_2$ solution adjusted to pH 4.7 with boric acid. Mercaptans and disulfide were purged with N_2 gas from the H_g complex into refrigerated pentane following acidification of the bubbler contents with 20% HCl. Organic solvent from the traps were combined, dried over anhydrous Na_2SO_4, and reduced to a suitable volume for gas chromatographic analysis.

The instruments used for analysis were a Tracor Model 550 and Tracor Model 560 Gas Chromatograph. The Model 550 is equipped with both a flame ionization detection (FID) and flame photometric detection (FPD) capability. An in-line 394 μm filter was used for operation of the FPD in a sulfur specific mode. FID is sensitive to carbon containing compounds. A standardization study was initiated to evaluate the detector response as measured in integration units (IU) relative to the moles of carbon injected. A similar study was conducted for sulfur containing compounds. Compounds employed in this effort and detector response corresponding to the instrument and detector employed are given in Table 12, while it should be noted that the technique quantifies material concentrations relative to carbon and sulfur only and underestimates the total mass. This technique is superior to those which quantify by either peak triangulation or inclusion of a single reference standard when dealing with unknown mixtures.

Table 12. Sulfur Compounds and Hydrocarbons Employed in Detector Response Study.

	DETECTOR RESPONSE	
	Flame Ionization	Flame Photometric
Hydrocarbon	IU*/mole of Carbon x 10^{12}	IU*/mole of Sulfur x 10^{13}
Anthracene	1.3	
Biphenyl	1.3	
Dibenzothiophene	1.4	3.8
Fluoranthene	1.5	
n-Hexadecane	1.4	
n-Hexacosane	1.5	
Napthalene	1.4	
n-Phenyls Carbazole	1.3	
o-Terphenyl	1.4	
Tetraphenylethylene	1.3	
1, 3, 5-Triphenylbenzene	1.3	
Triphenyl methane	1.4	
Xanthene	0.9	
-Butyl mercaptan		3.2
n-Hexyl mercaptan		4.3
n-Heptyl Mercaptan		4.4
Diethyl Sulfide		6.4
Diallyl Sulfide		6.1
Di-n-butyl Sulfide		5.2
Carbon Disulfide		3.8

*IU = Integration units.

Both GC's were fitted with 6 ft. (2.4 cm) by 1/4 in. (0.6) I.D. glass columns packed with 3% OV-1 on 80/100 mesh Chromosorb-W. The Model 550 was operated at a column temperature program between 86 and 464°F (30 and 240°C) at 1.7°F (3°C) per minute with an initial hold and final hold of 8 and 20 minutes, respectively. In general, the Model 550 was used to screen for sulfur containing compounds, and the Model 560 was used to screen for higher molecular weight hydrocarbons. The Model 560 column temperature was programmed between 212 and 464°F (100 and 240°C) at 5.4 °F/min (3°C/min) with an initial hold setting of 10 minutes and final hold of 40 minutes.

Quality control was maintained with daily monitoring of column efficiency and detector response. This was accomplished by injecting standard mixtures with widely varying retention times. The standard mixture was formulated from commercially available materials of high purity. Commercially available, standard compounds, similar to those expected to occur as emissions from asphalt were used in preparing the mixtures. These compounds were reasoned to be structurally similar moieties of asphalt, formed by thermal fragmentation and/or by reaction with sulfur during formulation of the various blends at high temperatures.

A combination GC-mass spectrometric analysis was made of the emissions from the highest sulfur containing mix design (MD-3) formulated at 350°F (176°C), and the control (i.e., no sulfur added).

Total sulfur was analyzed by the LECO Combustion Method whereby sulfur is oxidized in an induction furnace to SO_2, transferred to the LECO 532 Automatic Titrator and measured by idometric titration. Several NBS sulfur standards were used to calibrate the buret against known quantities of sulfur. Samples of unknown sulfur content are than assayed by comparison techniques.

3.1.2.3 Summary of Emissions Generated During Mix Preparation

Inorganic Emissions

Concentrations of H_2S and SO_2 emitted during the preparation of seven mix designs (MD 1-7) at 250, 300 and 350°F (121, 149 and 176°C) are shown in Tables 13a and 13b. Table 13a shows the concentrations generated using the controlled volume mixing chamber shown in Figure 7. The data shown in Figure 13b reflect the concentrations generated in the open atmosphere of the laboratory. The latter represent the peak concentrations which always occurred 5 seconds and 15 seconds after introduction of the sulfur and asphalt to the mix.

Examination of Tables 13a and 13b indicate the following:

1) The emissions collected in the closed environment were significantly higher than those taken under the more job-simulative conditions of the laboratory.
2) Peak load concentrations decay by an average factor of about five between 5 and 15 seconds after initiation of mixing.
3) Both H_2S and SO_2 emissions increase with temperature and with the rate of evolution once the temperature exceeds 300°F (149°C).
4) When mixes in the controlled environments are held at temperature above 300°F (149°C), the emissions rapidly approach and then exceed the MAC values for both H_2S and SO_2.
5) The emissions, where detectable, relative to the seven sulfur-asphalt mix designs appeared to be in the same proportions for both the closed and laboratory environments.
6) The high concentrations which appeared in MD-4 (recycled mix with no sulfur added) in both the controlled and laboratory test can not be explained. The fact that below 300°F (149°C) the H_2S emissions are about the same as for MD-5 (recycled with 1.0 percent sulfur added), indicate

Table 13. Variation of Gaseous Emissions with Mix Temperature As Generated During Mix Formulation.

Controlled Environment - Figure 13a

Gaseous Vapor	Temperature °F (°C)	Mix Design Number* 1	2	3	4	5	6	7
		Concentration, ppm						
H_2S	250 (121)	3.5	15	12	10	9	0.5	2.0
	300 (149)	8.0	280	305	110	90	2.0	78.0
	350 (176)	173.0	620	595	1100	500	2.5	385.0
SO_2	250 (121)	4.0	8.0	6.0	10	0.4	0.5	1.0
	300 (149)	9.0	140.0	160.0	39	83.0	2.0	17.0
	350 (176)	87.0	361.0	245.0	550	250	2.0	187.0

Laboratory Environment - Figure 13b

Gaseous Vapor	Temperature °F (°C)	Mix Design Number* 1	2	3	4	5	6	7
		Concentration, ppm						
H_2S 5 sec (15 sec)	250 (121)	Tr	Tr	1.1	Tr	>0.1	0.5	Tr
	300 (149	2.5 (Tr)	1.5 (Tr)	3.0 (Tr)	1.7 (Tr)	2.0 (Tr)	1.0 (Tr)	3.0 (>0.1)
	350 (176)	50 (7.0)	5 (1.5)	65 (14)	20 (5.0)	25 (5.0)	1.5 (0)	22 (3.0)
SO_2 5 sec (15 sec)	250 (121)	← (Tr) (0) →						
	300 (149)	1.5 (Tr)	1.0 (0.3)	1.0 (0.1)	.5 (0)	1.7 (Tr)	1.2 (0.3)	0.4 (0)
	350 (176)	23 (4.0)	2.8 (2.0)	33 (7.8)	8 (2.0)	13 (2)	1.5 (Tr)	7 (1.5)

*Mix designs and numbers are given in Table 11, page 39 residual sulfur may have existed in the original unprocessed material.

7) The influence of DCPD in the sulfur concrete is discussed in Section 3.1.6.

Emissions are of approximately equal ratios of H_2S:SO at a formulation temperature of 250°F (121°C). At the highest formulation temperature of 350°F (176°C), a 2:1 ratio of H_2S:SO_2 was observed. It should be noted that the values represent peak concentrations observed and several factors such as the rate of heating may have affected the results. Although settings for the heating mantle were maintained, the same throughout the experiment, the different mix designs affected heating rates. Temperature differential across the samples thus resulted in less than definitive observations between mix designs, other than to point out the asphalt along released insignificant quantities of H_2S and SO_2 at even the highest formulation temperature.

In order to make comparisons between mix designs, the total H_2S and SO_2 emitted was expressed in a flux term (F) by dividing the total quantity of each gas emitted by the sample mass (M) and the time interval (t) for which the mix was heated; $F = \frac{Q}{Mt}$. The time interval employed varied not only between mix designs but within a single mix design relative to the formulation temperature. However, a minimum 10 minute reaction interval was employed to better validate the flux. Obviously a higher flux term corresponds to a higher emission level over longer time interval.

Flux values are presented in Table 14 and 15. The data suggest that similar masses of H_2S and SO_2 are emitted at corresponding formulation temperature for a given mix design. Vapor flux values are approximately equivalent at the highest mix temperature with the exception of the high-sulfur mix design (MD-3) and control (MD-6). Although the peak

Table 14. Variation of Vapor Fluxes of H_2S and SO_2 with Respect to Mix Temperatures Generated During Mix Formulation.

Vapor	Temperature		Mix Design*						
			1	2	3	4	5	6	7
	°F	(°C)	mg/kg/min						
H_2S	250	(121)	4	18	9	12	1	1	3
	300	(149)	9	260	114	26	42	2	90
	350	(176)	120	294	552	255	232	3	356
SO_2	250	(121)	9	14	5	22	1	1	3
	300	(149)	114	176	92	47	40	4	38
	350	(176)	240	267	610	240	218	4	326

*Mix designs and numbers are given in Table 11, page 39.

Table 15. Variation of Vapor Flux Values for MD-3 As Affected by Atmosphere.

	Temperature		Vapor Flux (mg/kg/min)	
	°F	(°C)	H_2S	SO_2
Air Dry	240	(121)	9.3	5.4
	300	(149)	114	92
	350	(176)	552	610
Air Wet	250	(121)	63	30
	300	(149)	320	531
	350	(176)	440	526
N_2 Dry	250	(121)	7.6	1.3
	300	(149)	417	234
	350	(176)	648	610

concentrations of H_2S and SO_2 for the MD-3 sample were equivalent to or lower than the other mix designs (Table 13), the concentrations were sustained for a longer time interval, due to the fact that MD-3 contained 5 to 8 times more sulfur in the mix initially. This resulted in larger H_2S and SO_2 flux values for the MD-3 material.

Comparisons of vapor flux values for MD-3 under different conditions are presented in Table 15. The increase in vapor flux with a corresponding increase in temperature was statistically significant at the 1% level. Although there were no statistically significant differences between vapor flux values with respect to atmospheric condition, the moist air (95% relative humidity) resulted in numerically higher H_2S and SO_2 emissions at lower temperatures. A statistical evaluation of the H_2S and SO_2 flux values using a "paired t" test suggested no difference in the magnitude of these fumes at corresponding mix temperatures and atmospheric conditions. No attempt was made to study atmospheric conditions on vapor flux values of the other mix designs due to negative results obtained on the high sulfur mix design.

A more thorough study of the high sulfur MD-3 material was made in a effort to mathematically model probable emissions levels relative to the mix temperature. Both H_2S and SO_2 gaseous emissions were described by an exponential function of the mix temperature (Figure 9). Regression coefficients approaching unity strongly suggest that temperature alone, if free sulfur is present in the mix, controls H_2S and SO_2 emission levels.

Sulfur trioxide was measured for all samples prepared at each of the respective mix temperatures. Only the high sulfur mix(MD-3) at the 350°F (176°C) mix temperature resulted in any measurable sulfur dioxide expressed as elemental sulfur (SO_2-S). Similarly, the SO_3-S flux value was 1.8 mg/kg/min.

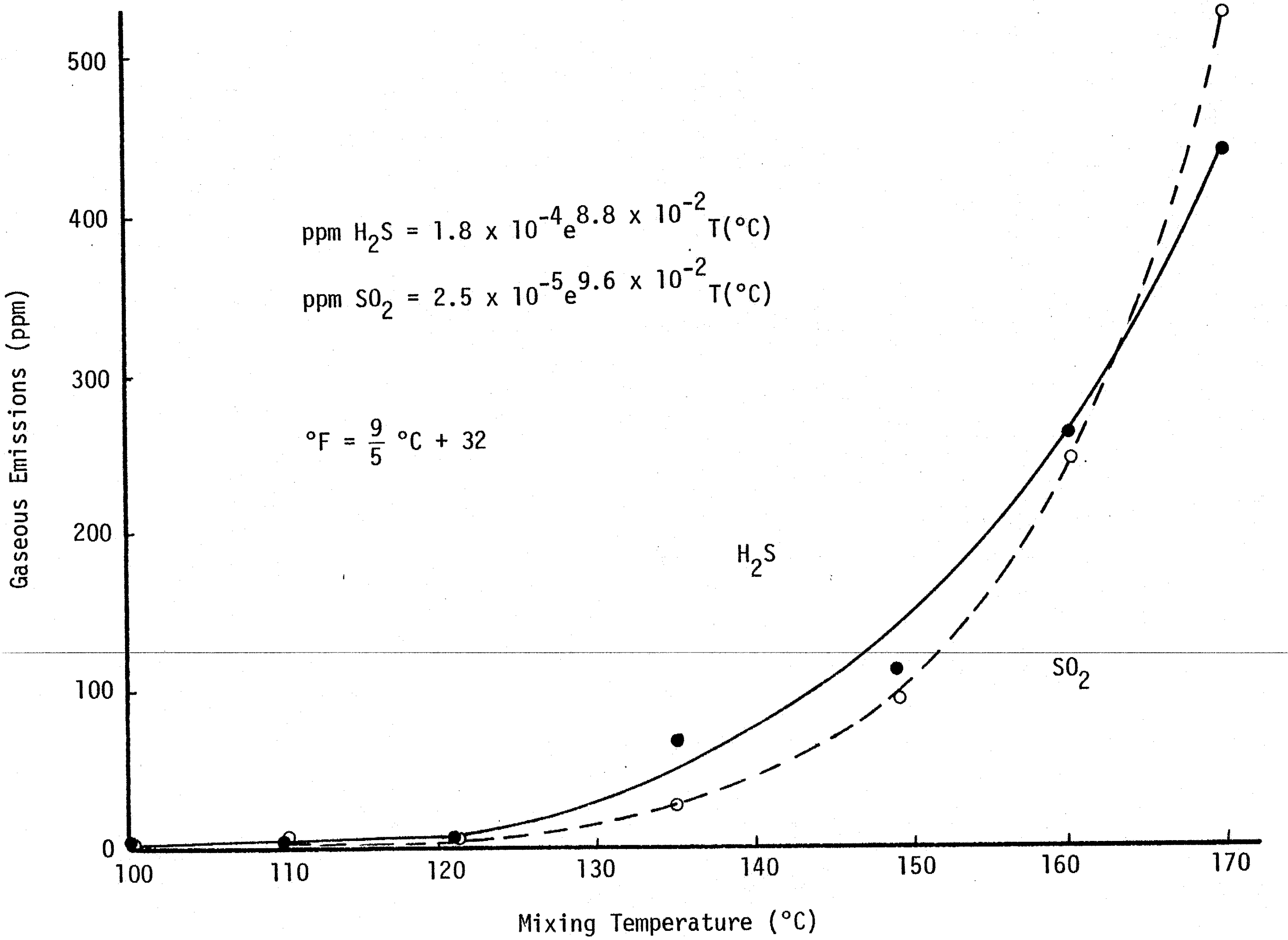


Figure 9. H_2S and SO_2 Emissions from MD-3 as Influenced by Mix Temperature - Controlled Environment.

Attempts to measure elemental sulfur were frustrated by unwanted deposition on apparatus surfaces which was impossible to recover and quantify. For this reason a mass balance was developed for sulfur in the various mix designs at the 3 mix temperatures. Elemental sulfur emissions were then estimated by the difference between total sulfur lost and the sum of that accounted for as H_2S, SO_2 and SO_3. Organic sulfur was too minute in quantity to have any effect on the material balance. The sulfur balance developed for the various formulations mixed at 250, 300 and 350°F (121, 149 and 176°C) are given in Table 16, 17, and 18 data. However, some organo-sulfur compounds of minute concentration may not be detected by FID, but show up as a large peak by FPD, due to the latter's much greater sensitivity.

Hydrocarbon emissions from mix designs formulated at 350°F are given in Figure 10. Two principles were used to determine which organic emissions, if any, would be considered significant. All emissions that can be attributed to normal asphalt are eliminated from consideration. This is not to imply that there is no hazard associated with these emissions, only that the scope of this work was limited to emissions induced by the use of sulfur. Also, organic emissions are not considered significant unless they exceed 1 ppm under the test conditions. Interpretation of the data according to these principles show no organic compound present in the emissions at the 1 ppm level. At the temperatures in the study no significant amounts of organic emissions, sulfur containing or otherwise, were detected above the normal to asphalt. FID scans of MD-2, MD-3, MD-4, MD-5, and MD-7, were developed following concentration to volumes suitable to detect 1 ppm of a $C_{11}H_{22}$ hydrocarbon relative to the total volume of air trapped. FID scans for MD-1 and MD-6 were concentrated more than required to demonstrate the similarities between characteristic GC profiles developed for a sulfur-asphalt mix and virgin asphalt.

Table 16. Sulfur Balance for Materials Mixed at 250°F (121°C).

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467.0	61.2	78.3	13.8	55.2
Residual	59.5	41.3	345.3	27.1	32.9	14.1	46.6
Total Emission	24.8	32.8	122.7	34.1	45.4	--	9.6
H_2S-S	0.1	0.5	0.4	0.4	0.2	--	--
SO_2-S	0.1	0.3	0.2	0.3	0.1	--	0.1
Total	0.2	0.8	0.6	0.7	0.3		
Elemental S	24.6	32.0	122.1	33.4	45.1	--	9.5

Table 17. Sulfur Balance for Materials Mixed at 300°F (149°C).

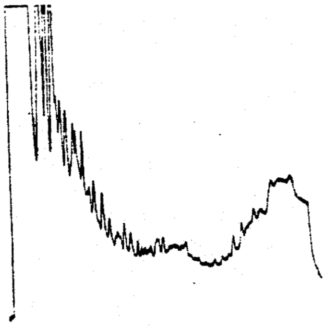
	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	25.7	23.4	314.3	22.9	29.4	12.4	45.7
Total Emission	58.6	50.7	152.7	38.3	48.9	1.4	9.5
H_2S	0.4	8.3	12.5	1.1	1.3	.1	2.7
SO_2-S	0.4	3.9	2.8	0.6	0.6	.1	0.6
Total	0.8	12.2	15.0	1.7	1.9	0.2	3.3
Elemental S	57.8	38.5	137.7	36.6	47.0	--	6.2

*Mix designs are given in Table 11, page 39.

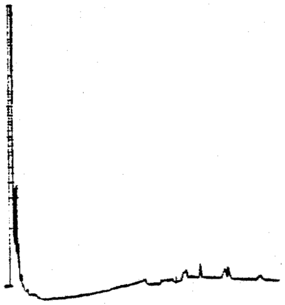
Table 18. Sulfur Balance for Materials Mixed at 350°F (177°C)

	Mix Design Number*						
	1	2	3	4	5	6	7
	Weight of Sulfur, mg						
Total S	84.3	74.1	467	61.2	78.3	13.8	55.2
Residual	18	24	207.5	18.7	26.1	13.6	40
Total Emission	66.3	50.1	259.5	42.2	43.3	0.2	15.2
H_2S-S	4.0	14.8	19.4	8.9	8.3	0.1	10.7
SO_2-S	2.1	7.5	9.2	4.2	3.9	0.1	4.9
SO_3-S	--	--	2.8	--	--	--	--
Total	6.1	22.3	31.4	13.1	12.2	0.2	15.6
Elemental Sulfur	60.2	27.8	230.9	29.1	31.1	0.0	0.0

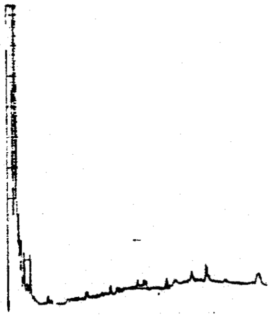
*Mix designs are given in Table 11, page 39.



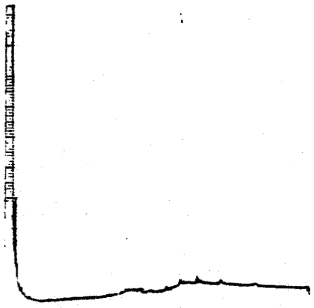
MD-1
2.7 ul
0.3 ml benzene
FID



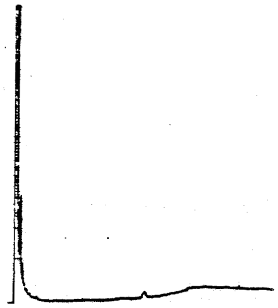
MD-2
2.7 ul
1.4 ml benzene
FID



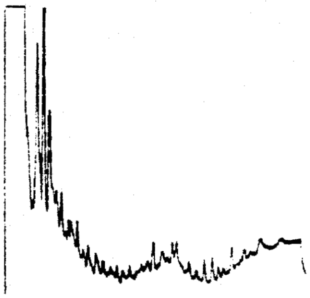
MD-3
2.5 ul
1.1 ml benzene
FID



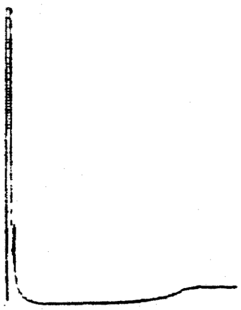
MD-4
2.6 ul
2.6 ml benzene
FID



MD-5
2.5 ul
1.6 ml benzene
FID



MD-6
2.5 ul
0.3 ml benzene
FID



MD-7
2.6 ul
3.3 ml benzene
FID

Figure 10. Hydrocarbon Emissions from Mix Designs Formulated at 350°F (177°C).

Although the concentrations may be slightly attenuated due to an extended formulation time interval relative to sample mass, and the total volume of air drawn through the traps, the tests are conservative considering the high temperature, and the fact that asphlatic emissions would be expected to be of higher molecular weight and carbon number. Heavier materials of greater carbon number would result in a greater detector response than that calculated for a 154 AMU ($C_{11}H_{22}$) hydrocarbon, respectively, It can be seen from this data that the bulk of sulfur lost during formulation will be as elemental sulfur, particularly at the lower mix temperature. Asphalt bound sulfur was retained by the sample at even the excessive mix temperature of 350°F (176°C) - MD-7, Table 18. Although total sulfur lost by the sulfur-asphalt mix designs increased with increased temperature, that loss as elemental sulfur was diminished, corresponding to increased H_2S and SO_2 emissions. A much lower percentage of sulfur incorporated in MD-7 was lost compared to the other sulfur asphalt materials, and all emissions were conserved as H_2S and SO_2 at 350°F (176°C). The open graded design used in the mix may explain in part the lower sulfur emissions observed for MD-7. Possibly the void space associated with the mix design has much poorer heat transfer qualities, reducing the total heated surface, or causing temperature differentials within the microfabric of the sample such that elemental sulfur vaporized is condensed on adjacent cooler particles surface. H_2S and SO_2 are gases and would tend to be less affected by heat differentials. The lower total sulfur emissions for MD-7 reflect the lower heat transfer properties of the mix design.

Organic Emissions

To improve efficiency, the refrigerated solvent traps were placed in an immediate in-line position to the reaction vessel and combined prior to volume reduction and gas chromatographic analysis.

Trapped emissions were first screened for hydrocarbons using the flame ionization detector system (FID), followed by a second chromatographic analysis using a flame photometric detector system (FPD) in the sulfur mode. Compounds containing carbon and sulfur will show in both at 1 ppm. Hydrocarbons containing sulfur would be less sensitive using FID, but would be detected by FPD due to its greater sensitivity.

Sulfur containing emissions were found to increase significantly with increased mix temperature for all but MD-6. The temperature effect is demonstrated for MD-3 in Figure 11. All mix designs with the exception of MD-6 responded similarly to temperature. A comparison of the FPD scans at the high mix temperature of 350°F (Figure 12) clearly demonstrates that the sulfur containing peak is independent of the asphalt used in the mix. Only the large peak is of significant magnitude, although numerous other sulfur compounds were detected.

The one sulfur containing compound present in significant amounts was identified as elemental sulfur. All available information supports this identification, and is summarized as follows:

1. There is no FID peak corresponding to the magnitude of the FPD peak, indicating that the material is not carbon containing.

2. The FPD scan is clean for the control, MD-6.

3. A mass spectrum of the emissions concentrated for MD-3 and MD-6 formulated at 350°F was made, and revealed a significant peak corresponding to a mass/charge ratio of 32 percent for MD-3 but not for the MD-6.

4. An attempt was made to isolate any mercaptans by complexing with Hg^{+2} and partitioning the complex in water. The aqueous solution of the complex is separated and acidified to disrupt the complex. Mercaptans are then partitioned into a benzene phase, which was concentrated and analyzed by GC using the FPD mode. The chromotograms were clean suggesting the peaks found previously were not mercaptans.

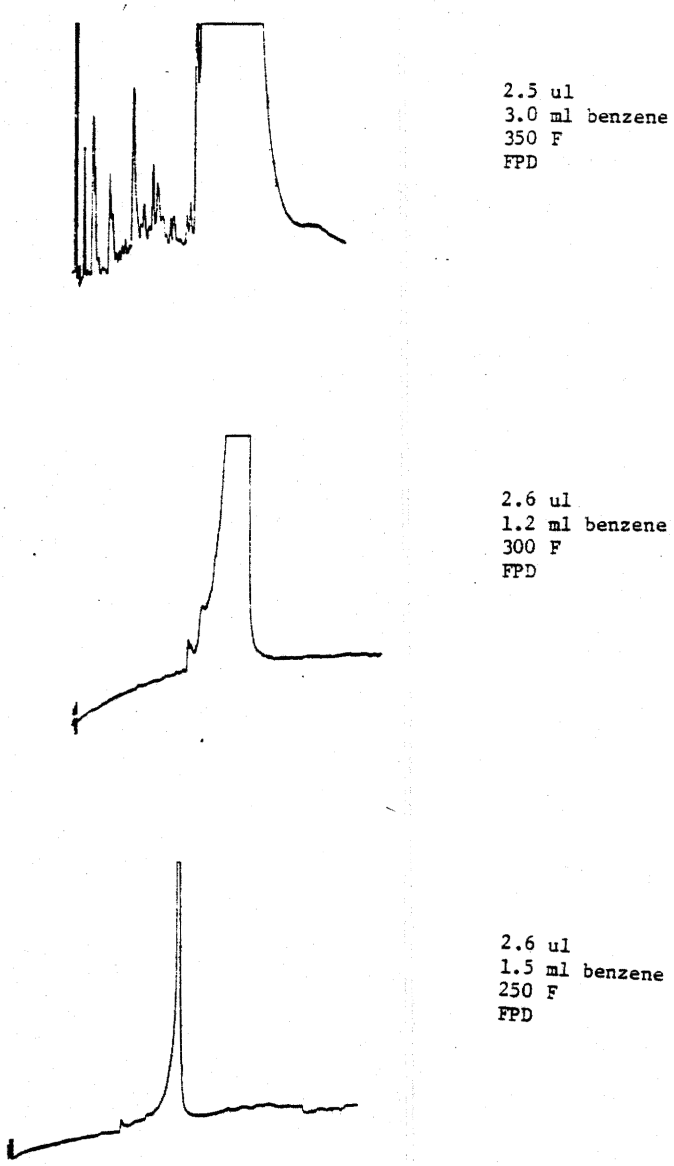
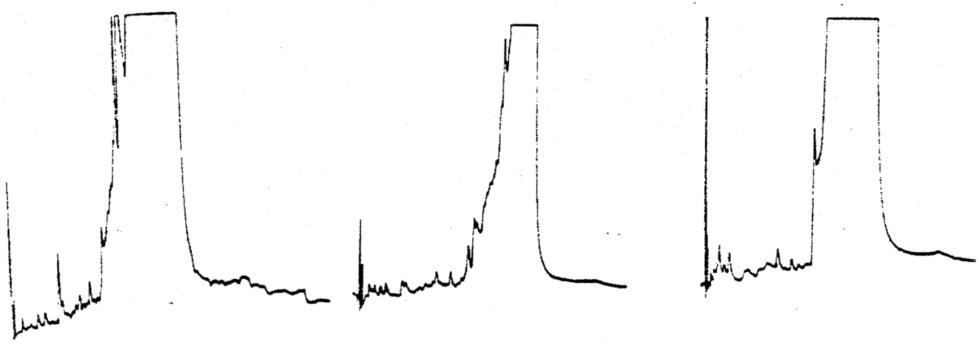


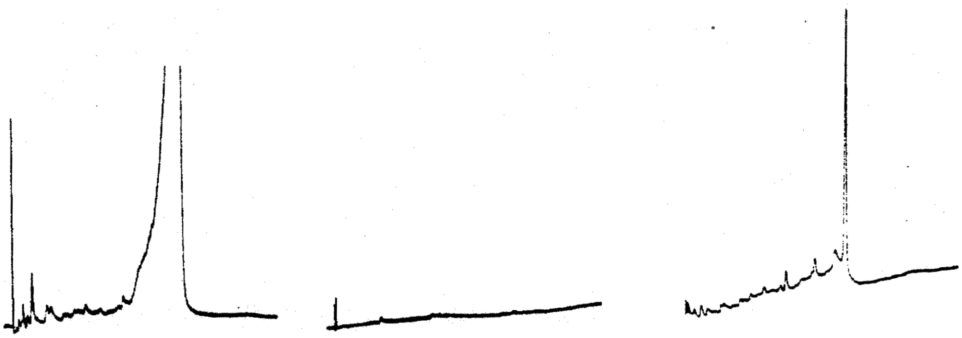
Figure 11. Sulfur Containing Emissions at 250, 300 and 350°F (121, 149 and 177°C) for MD-3.



MD-1
2.4 ul
1.4 ml benzene
FPD

MD-2
2.6 ul
2.0 ml benzene
FPD

MD-4
2.5 ul
1.8 ml benzene
FPD



MD-5
2.6 ul
3.3 ml benzene
FPD

MD-6
2.6 ul
3.0 ml benzene
FPD

MD-7
2.4 ul
2.5 ml benzene
FPD

Figure 12. Sulfur Containing Emissions at 350°F (177°C) for MD-1, MD-2, MD-4, MD-5, MD-6 and MD-7.

In summary, H_2S and SO_2 are produced in potentially lethal concentrations during formulation of sulfur-asphalt only when temperatures exceed 320°F (160°C) and when maintained in a closed environment such as that of heated storage silo. Concentrations of both gases will rapidly diminish under the open air conditions associated with the paving process.

Of greatest environmental concern is the vaporous elemental sulfur released during the dumping and paving process. Upon cooling the vapors will condense into fine particulates, which could be deposited on adjacent foliage and soil surfaces. Fines may also be transported from the pavement surface by wind, or in runoff following a rainfall event. Elemental sulfur would have an acidifying affect following any chemical and/or biological oxidation. The net impact will largely be determined by the buffer potential of soils and surface water affected. Maintenance of paving temperatures below 300°F (149°C) will reduce the potential of an adverse impact.

As will be discussed later, weathering of compacted sulfur-asphalt pavements by natural conditions is,at best,significant only in the long term. Concentrations of sulfur constitutents lost to the environment over a short term interval were found to be too low to have a measurable impact.

3.1.3 Weathering Studies

A series of tests were designed to assess the environmental and biological impact of sulfur modified pavements as caused by exposure to material weathering and simulated traffic wear. Sulfur induced fumes, dusts and runoff products were collected under a variety of in-service simulated environmental conditions including high temperatures, actinic light (UV radiation), simulated traffic wear, freeze-thaw cycling, rainfall, biological weathering, etc. These evaluations were made using two separate but complementary studies.

(a) Exposure to the elements of large scale (maximum surface area) pavement slabs.

(b) Analysis of runoff generated in simulated in-service conditions. In the first study (item a) slabs of pavement materials were exposed over a six month period including summer and winter months during which they experienced the combined effects of daily and seasonal temperature fluctuations, actinic light and rainfall. In the second study, small scale samples were evaluated using hydrolysis and mass balance techniques following exposure to each of the following four types of weathering conditions:

(a) High temperature
(b) UV radiation
(c) Freeze thaw
(d) Biological weathering

Seven mix designs numbered MD-1, 2, 3, 6, 7, 8 and 9 as given in Table 11 were used in these tests.

3.1.3.1 Exposure of Large Scale (Maximum Surface Area) Pavement Slabs

The temperature, actinic light and rainfall conditions were achieved by exposing slabs of selective mix designs on the roof of the six-story Soil and Crop Sciences, Entomology Center on the Texas A&M campus (Fig 13). The slabs were 2 ft. (61 cm) x 3 ft. (91.5 cm) x 2 in. (5 cm) thick cast into wooden frames, lines with aluminum to prevent any interaction between the wood and mixture ingredients.

A clear plastic box 1 ft. (30.5 cm) x 2 ft. (61 cm) x 0.5 ft. (15.3 cm) deep with a 2 in. (5 cm) diameter vent was constructed to fit over the slabs and provide a constant volume, controlled environment for emissions monitoring. Two 3.8 in. (1 cm) diameter ports (Fig 14) were drilled into the side of the box opposite from the vent to be used for sampling H_2S and SO_2 respectively. Air samples were monitored using Interscan monitoring devices. The vent was fitted with a 2 in. (5 cm) diameter x 39 in. (1 m)

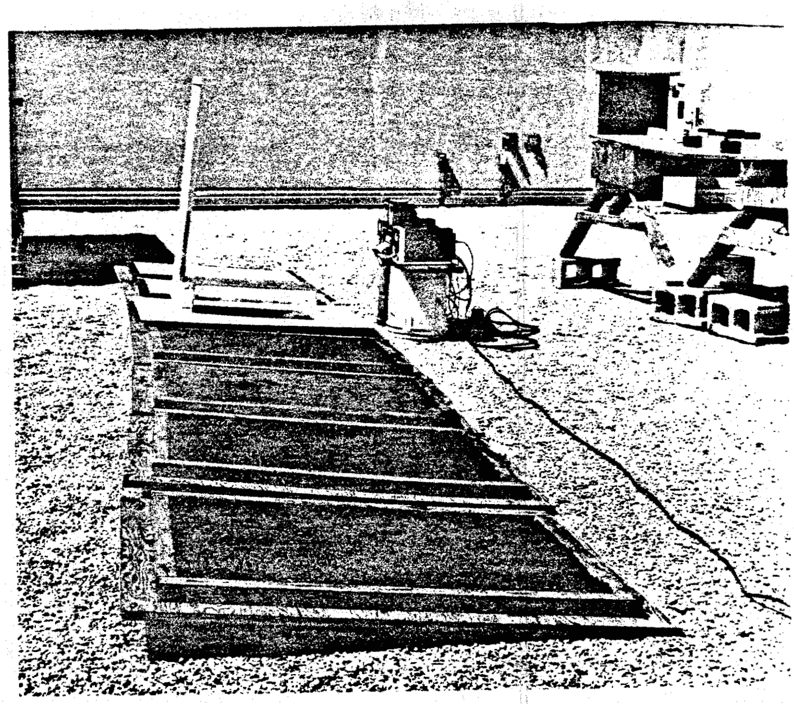


Figure 13. Pavement Slabs Under Exposure to the Elements for Weathering Studies.

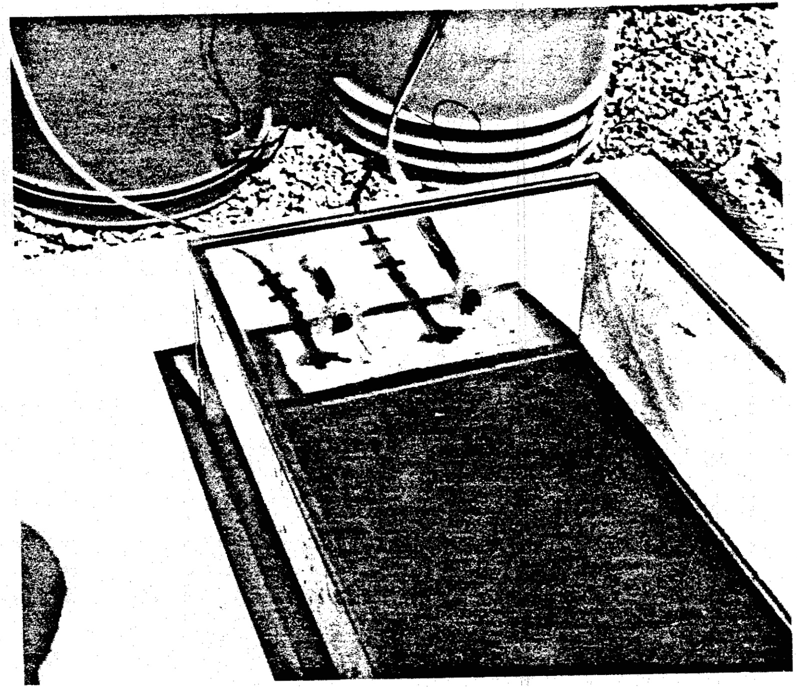


Figure 14. Exhaust Ports for Sampling H_2S and SO_2

long polyethylene stand pipe. This was to assure that air being drawn through the vent was not contaminated by emissions from adjacent slabs.

Surface temperature were measured using a copper-constantin thermocouple (Fig 15). Intimate contact between thermocouple and slab surface was maintained using transparent tape. After installation of the thermocouples, the plastic box, fitted with a white card board boarder, was placed over each slab and the surface temperature allowed to equilibrate. Outlets were combined then split 3 ways such that one air stream was drawn through an H_2S meter, one through an SO_2 meter, and the other through a series of refrigerated solvent traps. Air was drawn with a vacuum pump over the specimen surface, through each meter and solvent traps at a constant flow rate of 1 liter/min. Flow rates were controlled with calibrated flowmeters. The test set up is shown in Figure 16 with a close-up of the monitoring equipment shown in Figure 17.

Volatilized constituents were measured with respect to surface temperature and time following environmental exposure using 7 of the 9 mix designs given in Table 11. Measurements were made between 2 and 4 pm so as to effect a maximized surface temperature relative to daily and seasonal air temperature variability. A few air samples were drawn during the morning hours for evaluation at the lower surface temperatures.

A geometrically progressive sampling interval was employed to evaluate volatilized components with respect to time. Time-zero corresponded to initial sampling of air volatiles following exposure of pavement materials immediately after placement on the roof. Successive samples were collected at 1, 2, 4, 12 and 36 week intervals (June through December 1979).

Figure 15. Location of Thermocouple for Surface Temperature Measurements.

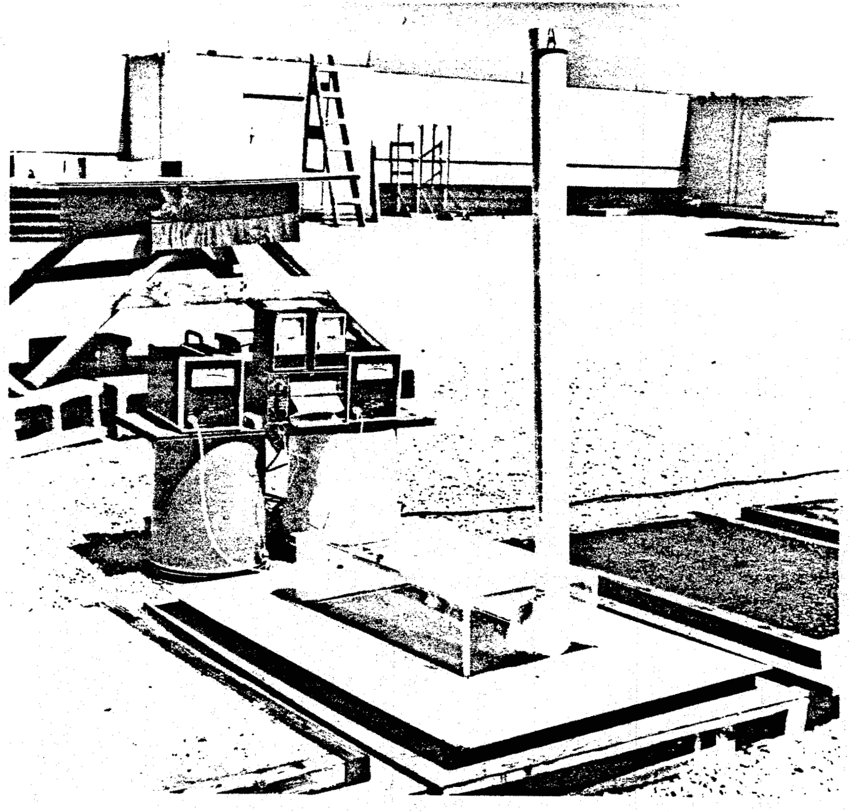


Figure 16. Weathering Test set-up for Exposure of Large Scale Pavement Slabs

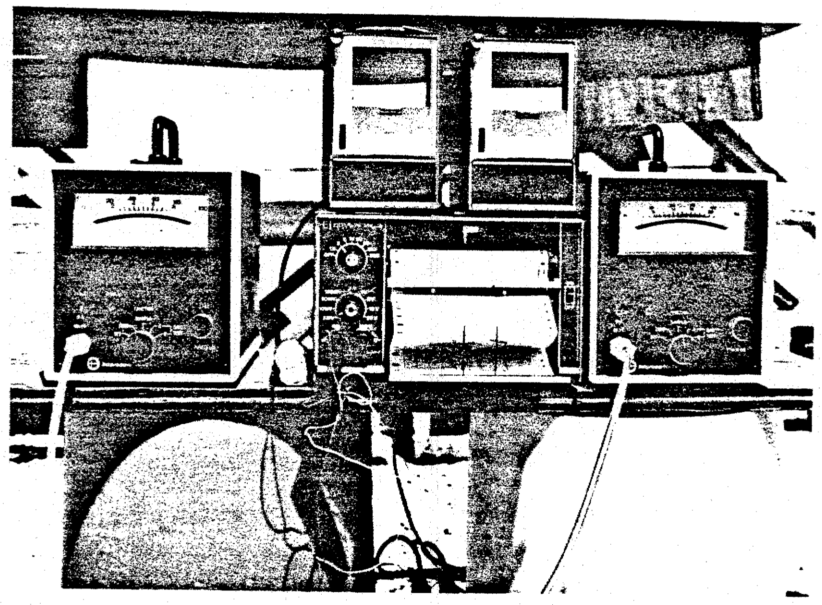


Figure 17. Close up of H_2S and SO_2 Monitoring Equipment Used In Weathering Studies.

Slab temperatures were monitored by continuously monitoring the output of the copper-constatin thermocouples. Output was calibrated against a mercury thermometer over temperatures ranging from 50°F to 212°F (10°C to 100°C), the range of surface temperatures anticipated.

H_2S and SO_2 emissions were monitored in ppm using Interscan Models 1176 and 1248, respectively. The meters were equipped with continuous strip chart recorders and were calibrated against commercially available span gases. Air samples drawn through refrigerated hexane traps were systematically screened by gas chromatographic analysis using a Tracor Model 550 GC equipped with flame ionization, and sulfur-specific flame photometric detector systems.

Solvents were dried over anhydrous Na_2SO_4 and reduced in volume by vacuum distillation prior to GC analysis. Generally, a 2.5 to 3.0 μ-liter sample was injected onto a 1/4 in. (0.6 cm) diameter x 6 ft. (183 cm) column packed with commercially available 3% OV-1 on 80/100 mesh gas chrom Q. Column temperatures were programmed to span between 86 and 464°F (30 and 240°C) at a 2.2°F/min (4°C/min.) rate. Detector response was measured by electronic integration of peak area. Integration units (IU) were assessed quantitatively by comparison with known quantities of reference material chromatographed at the same instrument settings. Analytical quality control was assured statistically by comparison of detector response to repeated injection of know hydrocarbons varying widely in molecular structure.

Inorganic and organic samples analyses were adjusted for background air quality as necessary. Meter readings in ppm by volume were normalized to volume at standard temperature and pressure to calculate moles of the respective gases volatilized relative to the total liters of air exhanged in the volatilization chamber. Vapor flux values were calculated by dividing the total gas evolved in milligrams by the surface area in square meters and the sampling time interval in hours.

Surface Temperature

The volatilization study was instigated during the first week of June 1979 and continued through the hot summer months to maximize the effect of surface temperature. Placement of the plastic box over the pavement resulted in a 15°F (8°C) increase in surface temperature due to a "greenhouse effect". Surface temperatures for the sulfur asphalt slabs generally ranged from 172 to 189°F (78 to 87°C), during the summer months, with the box in place. The maximum temperature recorded for the sulfur concrete material was 163°F (73°C) and 154°F (68°C) for sulfur concrete modified with dicyclopentadiene. Throughout the test, the surface temperature of DCPD-modified concrete was about 15 to 18°F (8 to 10°) cooler than the unmodified surface concrete.

Inorganic Sulfur Fumes

Once the box was placed on a slab specimen, the temperature recorder was turned on to determine an equilibrated maximum surface temperature. During the equilibration period, air flows were set through the meters and solvent traps without the volatilization chamber in line. Following the adjustment of flow rates to 1 liter/min., the background concentrations of H_2S and SO_2 were measured. Generally, pavement temperature was equilibrated to a maximum within 10 to 15 minutes, at which time the volatilization chamber was connected to the air flow lines.

A typical pattern for H_2S evolution continuously monitored with respect to time is shown in Figure 18. The concentration rose quickly to a maximum and then diminished to much lower levels, often that of the background air drawn into the volatilization chamber. The decline in concentration was attributed to a decrease in surface temperature as the cooler air passed over it. The pattern also suggests that vapor flux values, ultimately calculated from the total μ-liter gas evolved, are inflated due to permeation into a closed system.

H_2S and SO_2 vapor flux with respect to time for an asphalt pavement with no added sulfur is given in Table 19. The data demonstrate a relatively small net flux from sulfur-asphalt mixes. The same asphalt was used in the sulfur-asphalt systems. Corresponding vapor flux values for mix designs with approximately 2% added sulfur are given in Tables 20, 21, and 22 for the AAS-Limestone (MD-1), SEA-Limestone (MD-7), and SEA-Open graded (MD-2) systems, respectively. All demonstrated initially higher H_2S vapor flux over that of the asphalt pavement. Only the initial SO_2- vapor flux for the AAS-Limestone (MD-1) and AAS-Sand (MD-3) systems (Tables 20 and 23) exceeded that of the control, (MD-6) material (Table 19). Vapor flux for both H_2S and SO_2 was diminished to base detection levels within 2 to 4 weeks following placement on the roof. Flux values measured during the morning hours were either too low for meter detection or at the sensitivity level. Sensitivities level. Sensitivities varied somewhat, depending upon the surge characteristics of the scan as developed from continuous recording of the detector response. However, it should be noted that lower morning vapor flux values reflect the correspondingly lower surface temperatures as compared to that achieved in the afternoon sun.

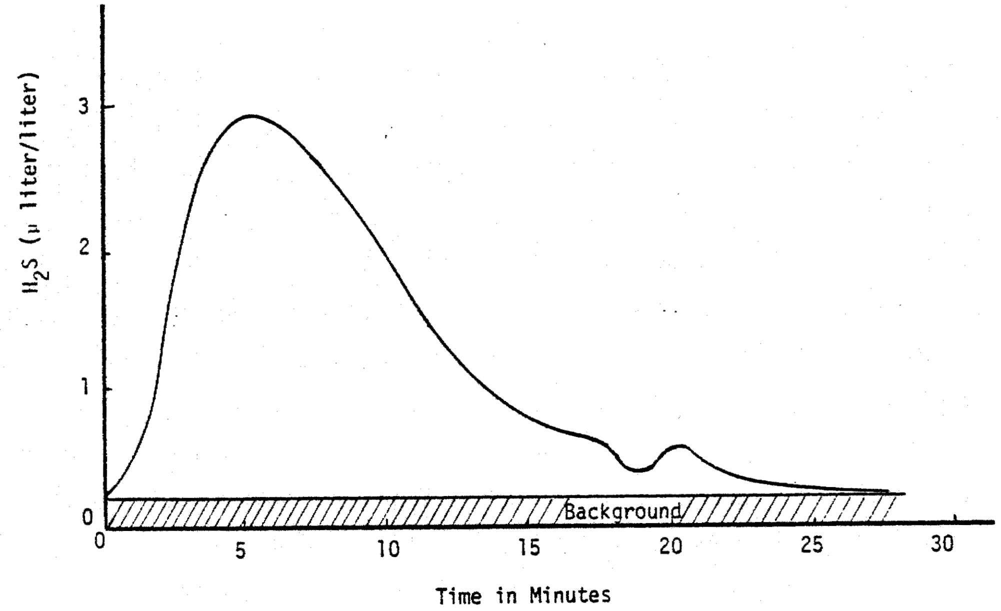


Figure 18. Typical Pattern of H_2S Evolution as Continuously Recorded with Respect to Time.

Table 19. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-6 (See Table 11, page 39).

Time	Surface Temperature		Vapor Flux H_2S	SO_2
weeks	°F	(°C)	μg/m^2/hour	
0	167	(75)	38.7	153
1	176	(80)	37.8	142
2	176	(80)	<37.8	< 74
4	172	(78)	ND	ND
12	169	(76)	ND	ND
24	86	(30)	ND	ND

Table 20. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-1 (See Table 11, page 39).

Time	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	μg/m²/hour	
0	181	(83)	262	352
1	181	(83)	119	140
2	185	(85)	75	69
4	178	(81)	< 37.7	< 71
12	172	(78)	ND	ND
24	86	(30)	ND	ND

Table 21. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-7 (See Table 11, page 39).

Time [1]	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	μg/m²/hour	
0	181	(83)	165	135
1	189	(87)	147	138
2 (pm)	187	(86)	75	70
(am)	154	(68)	< 39	< 70
4	185	(85)	37.1	69
12 (pm)	181	(83)	< 37.0	< 71
(am)	113	(45)	ND	ND
24	122	(50)	ND	ND

[1] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 22. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-2 (See Table 11, page 39).

Time [1/]	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	$\mu g/m^2/hour$	
0	172	(78)	183	141
1	181	(83)	119	126
2	172	(78)	114	143
4 (pm)	172	(78)	< 38.2	< 73
(am)	144	(62)	ND	ND
12 (pm)	163	(73)	ND	ND
(am)	115	(46)	ND	ND
24	86	(30)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 23. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for MD-3 (See Table 11, page 39)

Time [1/]	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	$\mu g/m^2/hour$	
0	181	(83)	955	872
1 (pm)	185	(85)	778	707
(am)	154	(68)	---	75
2 (pm)	189	(87)	637	699
(am)	169	(76)	462	435
4 (pm)	181	(83)	281	284
12 (pm)	181	(83)	150	141
(am)	158	(70)	< 39	< 74
24 (pm)	113	(45)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

The higher sulfur containing AAS-Sand mix (MD-3) produced considerably higher H_2S and SO_2 vapor flux values (Table 23). However, values were rapidly diminished to those approximating the initial flux values of asphalt alone with 12 weeks, which suggests that the vapor flux is dependent upon a surface temperature induced loss mechanism by volatilization, but that losses are finite, and materially diminished with weathering of the pavement surface.

Flux values for the sulfur concrete, perhaps best illustrate the temperature influence. Flux values for sulfur concrete and sulfur concrete plus dicyclopentadiene (Tables 24 and 25) were approximately equal in magnitude to those of the lower sulfur-asphalt pavement materials although they contained more than 10 times the total sulfur of the latter. Reduced flux values with time at comparable or higher surface temperatures demonstrated the attenuating influence of a weathered surface on H_2S and SO_2 evolved.

Organic Pollutants

At no time during the course of the volatilization study did vapors or fumes emanating from the pavement specimens exceed that of the background air quality with respect to organic or organic sulfur compounds.

At the end of 4 weeks, air samples were drawn separately for organic analysis in an attempt to increase sensitivity to organics. Thus all vapors from the chamber following temperature equilibration were passed through the refrigerated solvent traps for subsequent screening of volatile organics. A few samples were drawn into petroleum ether to determine if reduction of hexane volumes may have caused losses of more volatile organics. This effect, plus the ability to detect low levels of organics emanating in background air suggested that organics were simply not a significant constituent of the vapors drawn in the volatilization study.

Table 24. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for Sulfur Concrete - MD-8 (See Table 11, page 39).

Time[1/]	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	$\mu g/m^2/hour$	
0	154	(68)	159	201
1	163	(73)	156	231
2	163	(73)	78	136
4	158	(70)	39	77
12 (pm)	163	(73)	39	73
(am)	140	(60)	ND	ND
24	79	(26)	ND	ND

[1/] pm 2 to 4 pm afternoon readings; am 9 to 11 am morning readings.

Table 25. Variation of H_2S and SO_2 Vapor Flux with Temperature and Time for Sulfur Concrete Modified with Dicyclopentadiene - MD-9 (See Table 11, page 39).

Time	Surface Temperature		Vapor Flux H_2S	Vapor Flux SO_2
weeks	°F	(°C)	$\mu g/m^2/hour$	
0	142	(61)	164	232
1	154	(68)	199	300
2	153	(67)	120	150
4	144	(62)	82	115
12	140	(60)	41	77
24	79	(26)	ND	ND

Analyses of fumes during formulation temperatures for the various mix designs support these conclusions. Temperatures achieved during formulation which ranged from 250 to 350°F (121 to 177°C) exceeded the surface temperatures of the slab specimens yet resulted in comparatively low organic values relative to inorganic sulfur losses.

Although vapor flux values were still measurable up to 12 weeks following placement of the slab specimen on the roof, the impact of volatilization from these sulfur-asphalt test units was small relative to the magnitude of the flux term. It should also be noted that the samples were subjected to excessive surface temperatures, releasing fumes into a closed environment, prior to air withdrawal.

To put the magnitude of the flux values in perspective, consider that the 955 $\mu g/m^2/hour$ reported for the initial H_2S from the high sulfur-asphalt blend, corresponds to a volume concentration in air of 2.6 ppm which is 50 percent of the MAC.

3.1.3.2 Analysis of Runoff Generated by Simulated In-Service Conditions

HIGH TEMPERATURE AND UV-RADIATION

Compacted specimens of the nine mix designs (MD-1 through 9) were prepared for exposure to temperature and ultra-violet (UV) light. Asphalt and sulfur-asphalt specimens were formed into 4 inch (10 cm) dia. x 3 1/2 inches (9cm) thick disc. The two sulfur concrete materials were shaped into rectangular bricks. Each formulation was made in quaduplicate. Two from each mix design were selected at random and wrapped in aluminum foil to eliminate the impact of ultra-violet light. Samples were set on a table on the roof of the Soil and Crop Sciences Building and exposed to direct sunlight for 6 months including the hot summer months (See Figure 19).

Following a 6 month exposure the outer edges of the compacted

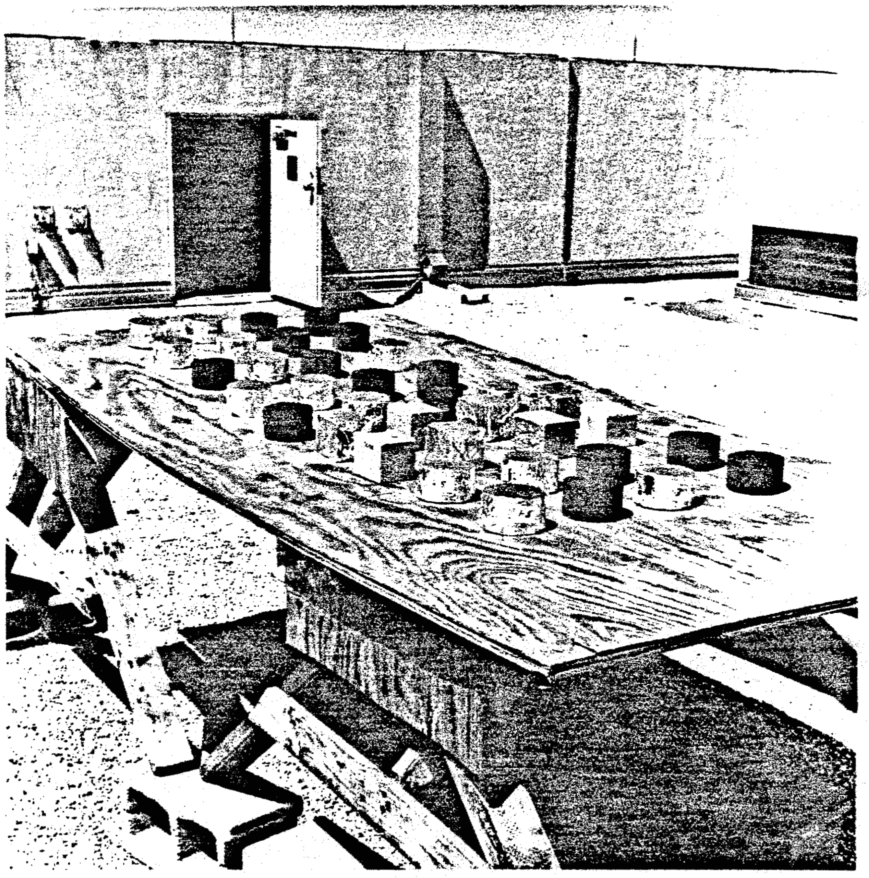


Figure 19. Samples Being Exposed to Ambient Temperature and Sunlight

specimens were chipped away using a hammer and chisel and subsequently ground in an ore crusher for total sulfur analysis. Materials were screened following the grinding process to give three size fractions; (a) that passing a 1 mm sieve (b) that retained on a 1 mm sieve but passing a 2 mm sieve, and (c) particles retained by the 2 mm sieve.

Total sulfur was determined for each mix design. Values obtained were utilized as a test statistics to determine the potential weathering affect of a combination high temperature and UV-light. In addition, the ground materials were subjected to both acid and base hydrolysis at a 187°F (86°C) reaction temperature to determine if a high temperature UV-light weathering combination resulted in subtle differences in emissions or hydrolysis products compared to laboratory control specimens.

Total sulfur relative to a particular mix design and exposure level to ultra violet radiation from full sunlight is summarized in Table 26. An Analysis of Variance (ANOVA) was carried out to aid interpreting the results. Initially, the variability between reps of sulfur concrete materials (MD-8 and MD-9) dominated as the greatest source of variation apart from MV design such that nothing could be interpreted for the sulfur-asphalt materials. A second ANOVA excluding the sulfur concrete data was determined, and results from this test given in Table 27. Results of this test show that reps were not significant, making definitive statements about the experiment relative to sulfur-asphalt possible.

Ultra violet radiation from full sunlight had no affect on the total sulfur measured. The greatest source of variation as one would expect was that of the mix design parameter due principally to the high sulfur content of AAS-Sand (MD-3) and low sulfur level of the control (MD-6). Surprisingly, results of the ANOVA revealed a UV-Light - Mix Design interaction which was statiscally significant at a 5% level. There was no distinct pattern in the data, and the only explanation for the interaction suggests that

Table 26. Total Sulfur of The Various Mix Designs Following Exposure to Full Sunlight at Normal High Surface Temperatures.

Exposure	Rep No.	Mix Design Number								
		1	2	3	4	5	6	7	8	9
		% Sulfur								
No UV-Light	1	3.1	2.0	15.1	2.4	2.8	0.4	1.6	21.0	36.3
	2	3.0	2.2	15.4	2.0	2.8	0.5	2.0	27.3	27.6
	Avg.	3.1	2.1	15.3	2.2	2.8	0.5	1.8	24.2	32.0
UV-Light	1	2.3	2.8	17.1	2.4	2.5	0.4	2.5	22.0	32.7
	2	2.6	2.3	15.8	2.9	2.4	0.4	1.5	28.4	28.8
	Avg	2.5	2.6	16.5	2.7	2.5	0.4	2.0	25.2	31.3

Table 27. Results of Analysis of Variance (ANOVA) For Mix Designs MD-1 through MD-7.

Source	Df	Sum of Squares	Mean Square	Fexp	F.01	F.05
Reps	1	0.481	0.481	4.45	9.07	4.67
Light (L)	1	0.241	0.241	2.23	9.07	4.67
Mix Design (No)	6	665.359	110.893	1026.78	4.62	2.92
LxMD	6	2.129	0.355	3.28	4.62	2.92
Error	14	1.398	0.108			
Total	27	670.144				

the samples randomly selected for exposure to sunlight had a slightly higher total sulfur content when processed.

Ground materials subjected to both acid and base hydrolysis reacted the same as the laboratory control samples, suggesting that actinic light gives no added inducement towards hydrolysis, or the effects are to subtle for the technique employed. The assessment was made relative to H_2S emission levels. No organics were detected in emissions trapped in refrigerated solvents, or dichloromethan extracts of filtered hydrolysates.

FREEZE-THAW TESTS

Compacted specimens for the 9 mix designs were subjected to the weathering impact of freeze-thaw cycling (ASTM C-666). The temperature of the cycle ranged from 0(-18) to 40°F (4°C), with each specimen subjected to a total of 100 cycles at 6 cycles per day.

Following the final thaw, the water used as the surrounding matrix was filtered and extracted by separatory funnel partitioning into 15% diethyl ether-dichloromethane. Extracts were dried over anhydrous Na_2SO_4 and reduced in volume to a very low volume then taken up to approximately 2ml with benezene. Aliquots were analyzed by gas chromatography using both flame ionization (FID) and flame photometric (FPD) detector systems.

The outer edges of the sample beam were chipped away from the bulk sample, ground to pass a 1 mm mesh sieve, and subsequently subsampled for total sulfur analysis. Subsamples were also subjected to acid base hydrolysis reactions to determine if freeze-thaw weathering results in enhanced chemical weatherability.

FID and FPD scans of freeze-thaw leachate waters partioned finally into benzene are given in Figures 20 and 28, for MD-1 through MD-9, respectively. Detector response to hydrocarbons (FID scans) suggests at first glance that there are significant quantities solubilized by freeze-thaw weathering. However,

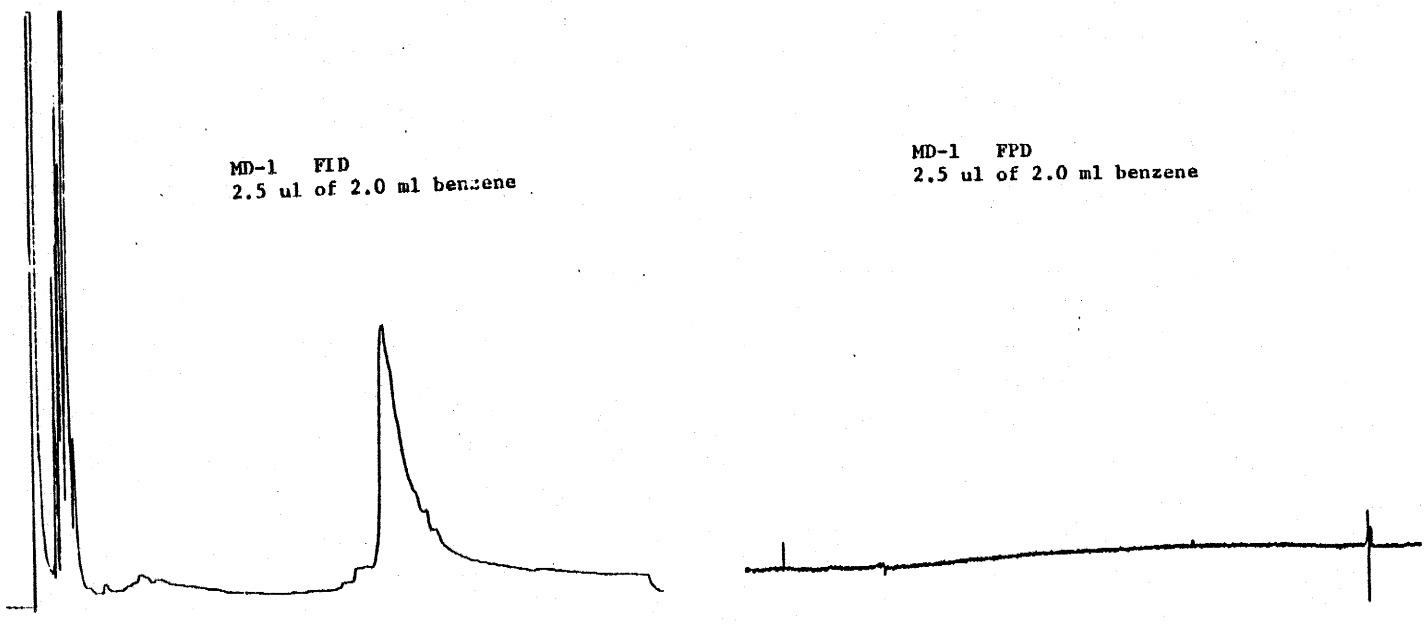


Figure 20. FID and FPD Scans for MD-1 Freeze-Thaw Leachates.

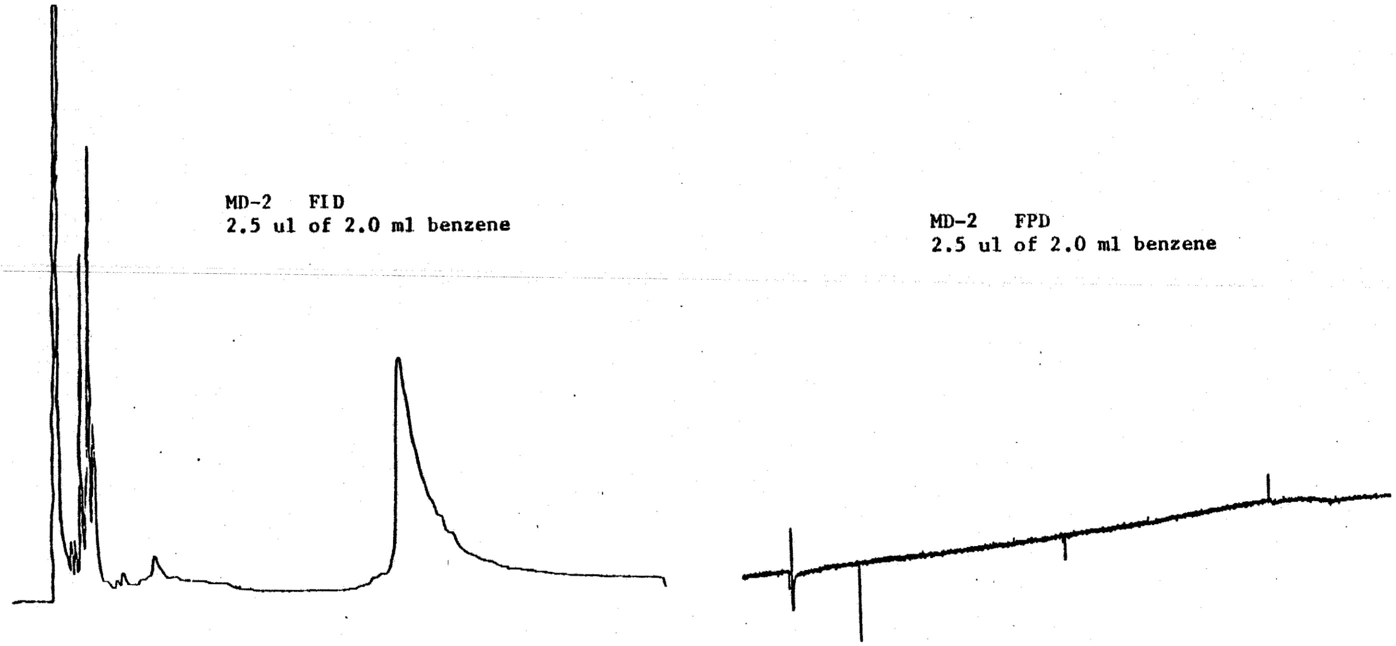


Figure 21. FID and FPD Scans for MD-2 Freeze-Thaw Leachates.

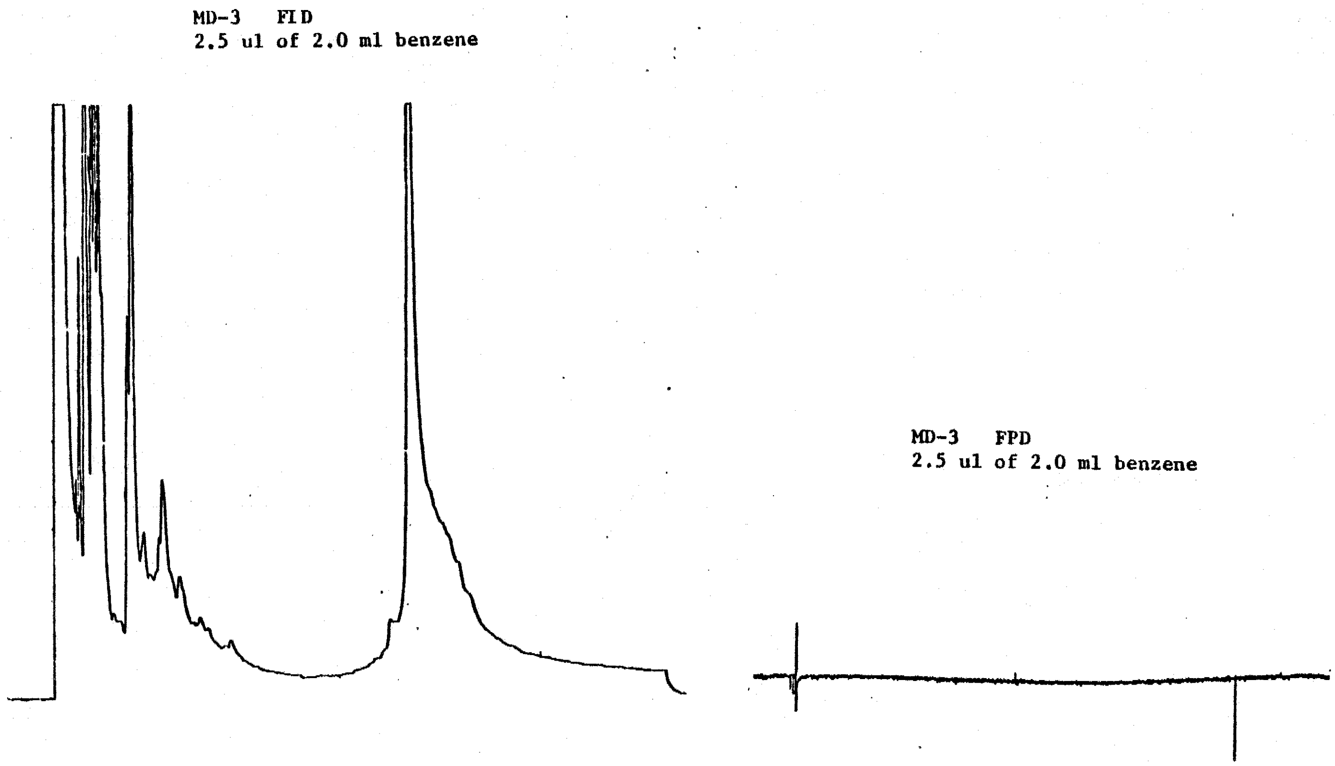


Figure 22. FID and FPD Scans for MD-3 Freeze-Thaw Leachates.

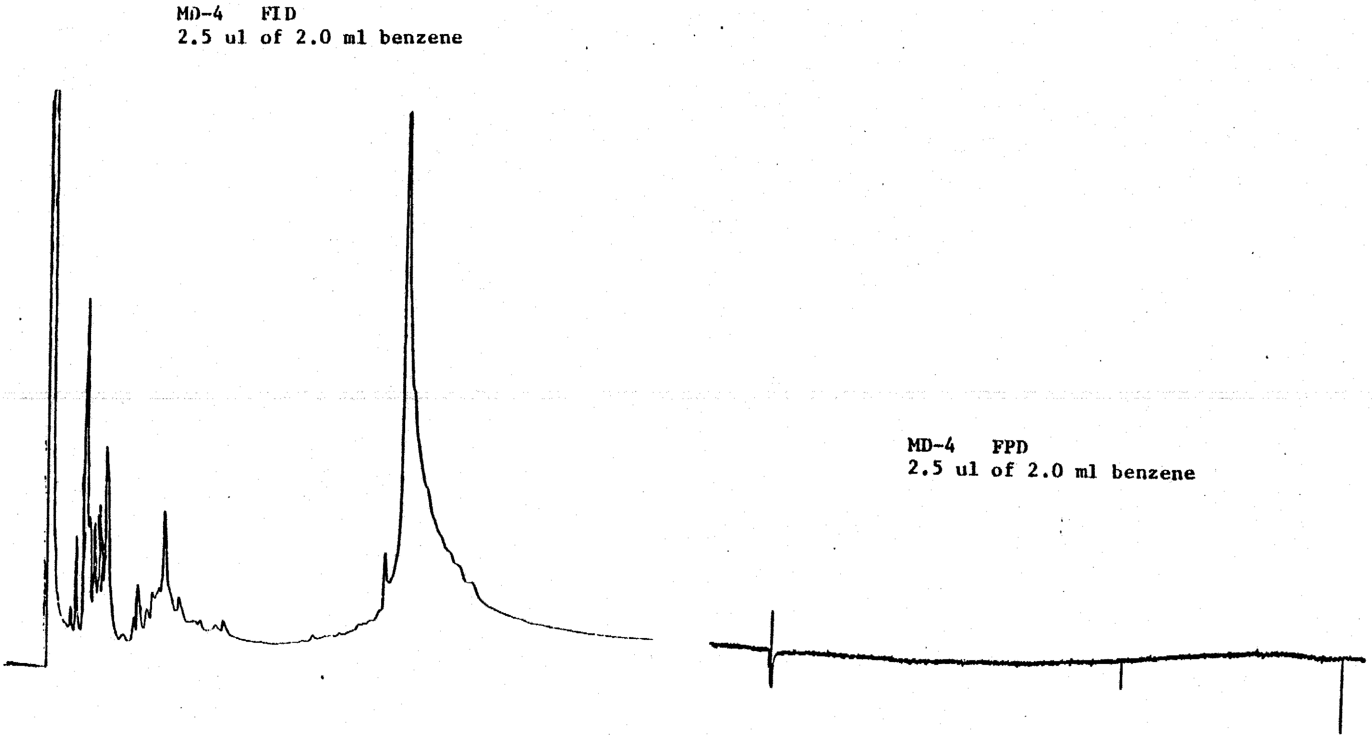


Figure 23. FID and FPD Scans for MD-4 Freeze-Thaw Leachates.

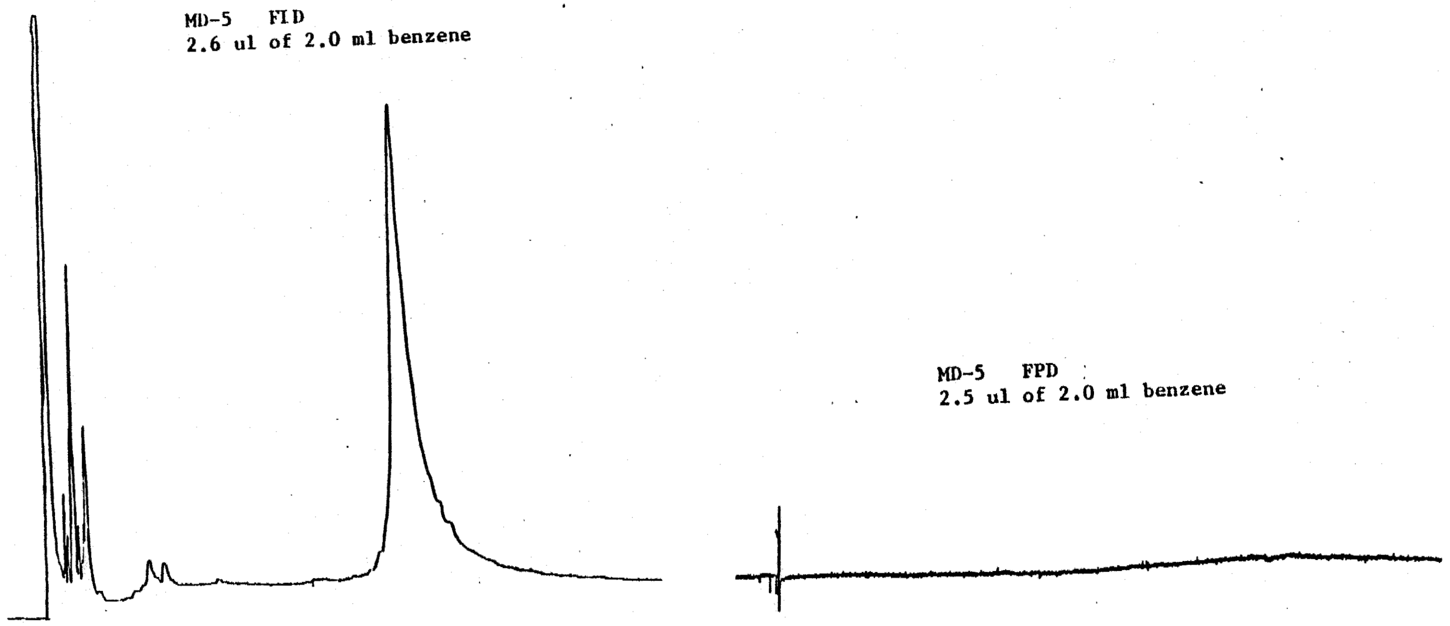


Figure 24. FID and FPD Scans for MD-5 Freeze-Thaw Leachates.

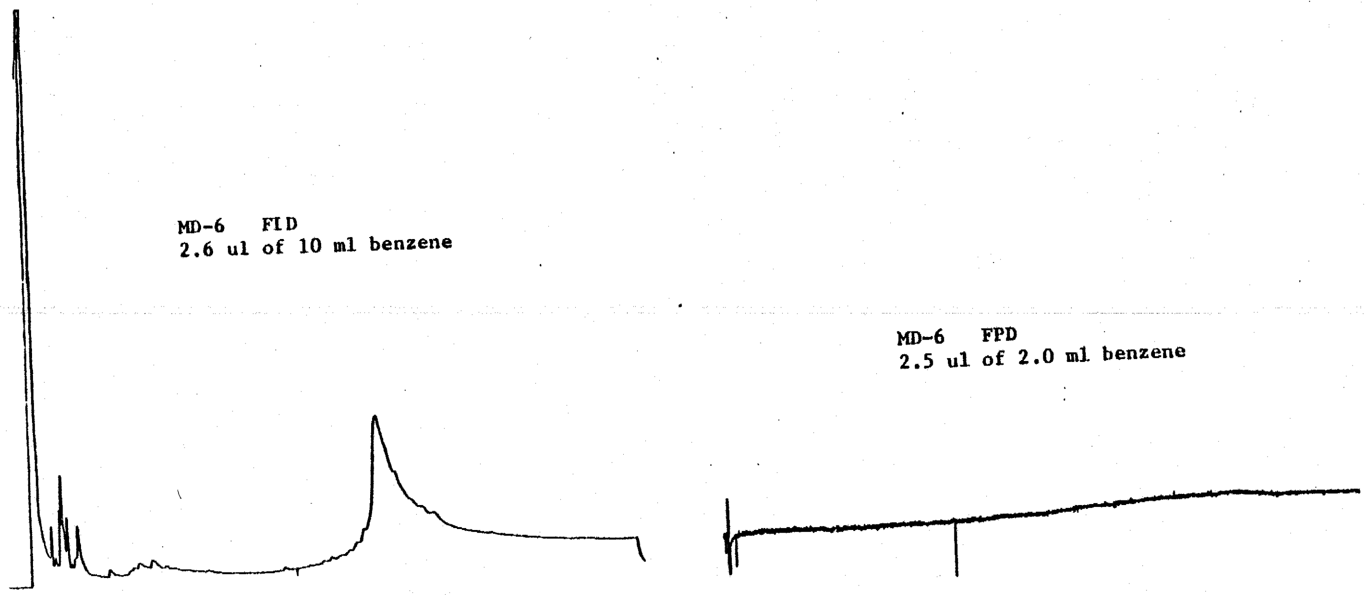


Figure 25. FID and FPD Scans for MD-6 Freeze-Thaw Leachates.

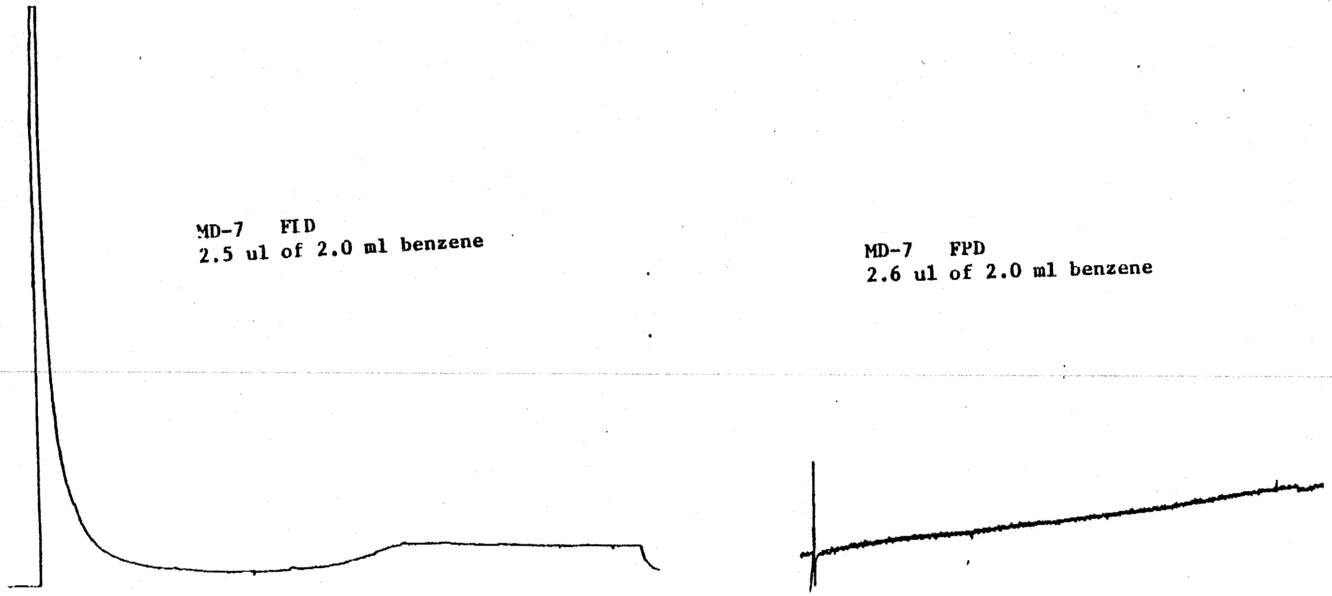


Figure 26. FID and FPD Scans for MD-7 Freeze-Thaw Leachates

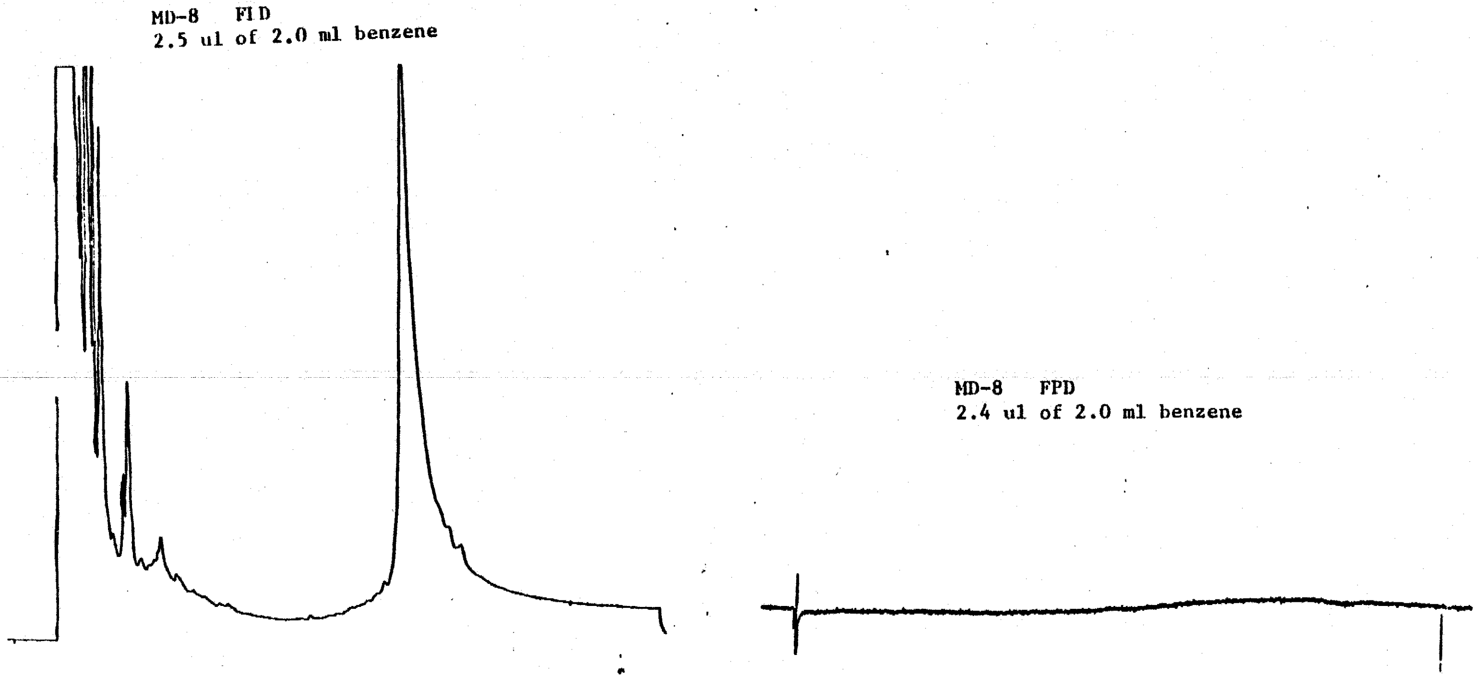


Figure 27. FID and FPD Scans for MD-8 Freeze-Thaw Leachates.

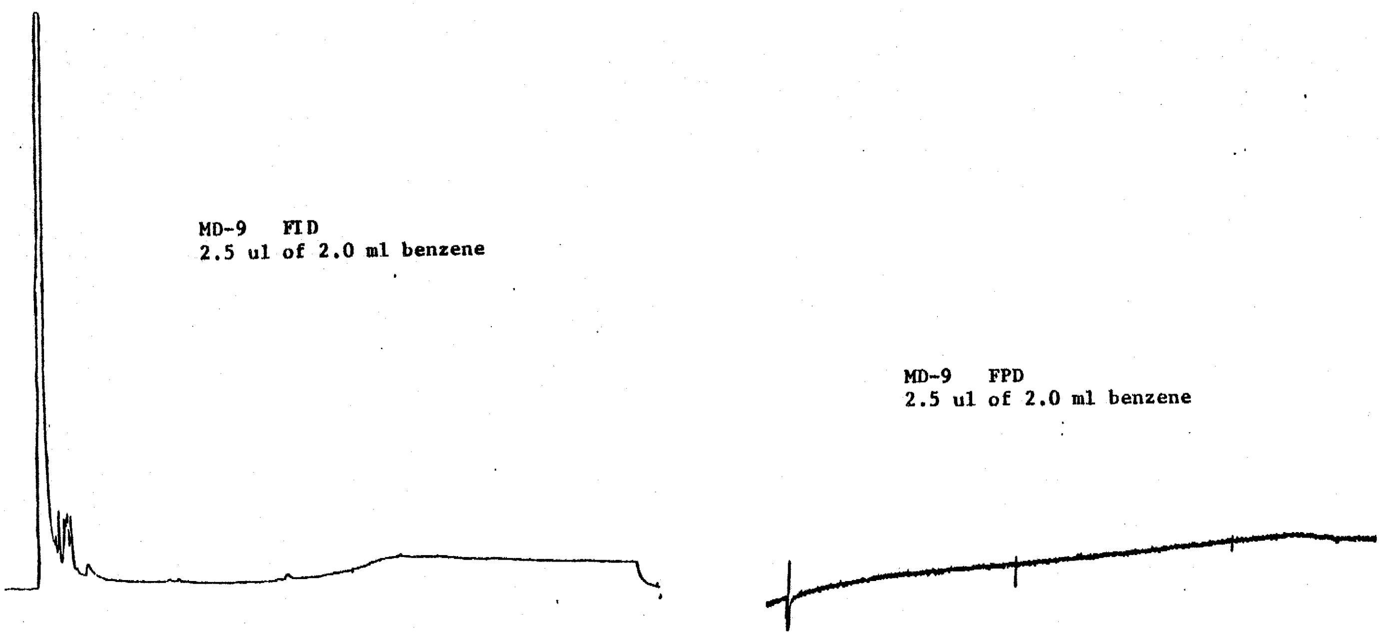


Figure 28. FID and FPD Scans for MD-9 Freeze-Thaw Leachates.

contamination appears to be a more logical explanation, due to the fact that even the sulfur concrete materials with no asphalt added reflected a significant FID detector response. FPD scans revealed that they hydrocarbons were not sulfur containing.

Samples chipped from the freeze-thaw beams and subjected to both acid and base hydrolysis reactions did not show any FID response, further supporting the conclusion that the leachate organics were actually freeze-thaw sample container contaminates and not sample constituents.

A total sulfur analysis (Table 28) suggested that there was no loss of sulfur from the sample following the multiple freeze-thaw weathering sequence.

Table 28. Total Sulfur Content of Compacted Specimens Following Freeze-Thaw Weathering.

	Mix Design								
	1	2	3	4	5	6	7	8	9
	% Sulfur								
Rep 1	3.12	2.90	17.0	1.87	3.02	0.42	2.02	25.44	18.62
Rep 2	2.68	1.56	15.7	1.98	2.42	0.57	1.93	22.50	18.90
Avg.	2.90	2.23	16.4	1.93	2.72	0.50	1.98	24.0	18.8

The difference between total sulfur values reported for MD-9 in the UV-light, high temperature study reported in Table 26, and those for the freeze-thaw test given in Table 28, resulted from sample treatment. Although materials from both studies were ground to pass a 1 mm mesh sieve, the freeze-thaw samples were ground to a powder prior to subsampling for total sulfur analyses. Rock fragments may have been excluded when subsampled in the previous study (Table 26) skewing the matrix towards sulfur particles, as indicated by a comparison to total sulfur reported for the MD-9 formulation.

With the exception for exhaust fumes which, it was felt, would have negligible effect on a sulfur-asphalt pavement, all the other conditions would manifest themselves in the creation of fine particles of dust through erosion or friction. This dust would eventually be blown by the wind or carried by rainfall run-off from the pavement to the soils or streams in the vicinity of the road.

It was decided that this dust could be created in the laboratory by grinding the test samples of the various mix design into 200 mesh particles and subjecting them to hydrolysis. The results generated would appear to be similar to those generated in the Freeze-Thaw tests. Since the basic ingredient being taken-off the road is elemental sulfur. The leaching effect on the rainwater would only have an effect on soils which have a low buffering capability. This can be offset by lime treatments. The potential for biological degradation is discussed in the next section.

SIMULATED TRAFFIC EFFECTS

There are numerous test apparatus which have been devised to evaluate pavement materials under simulated traffic conditions. The ensuing evaluations are usually made with respect to the materials structural integrity(i.e. rutting, fatigue life, etc). However, to the authors' knowledge no such test exists for specially evaluating the effect of traffic on the environment. The factors resulting from traffic which would impact the environment include:

(a) Skidding
(b) Snow plow friction
(c) Tire - pavement interaction
(d) Exhaust fumes

CHEMICAL HYDROLYSIS

Compacted specimens of the various mix designs were ground to pass a 2 mm mesh sieve. A 5 g sample was placed in a 500 ml reaction vessel, followed by 300 ml of pH 10 water. These extremes were selected as maximum potential weathering environments via chemical hydrolysis, that could result on the surface of an in-service pavement. The reaction vessel was heated to 185°F (85°C). Once the temperature was attained the hydrolysate solution was degassed with an airstream controlled at 1 liter/minute and continuous stirring. The airstream was passed through an H_2S meter.

Hydrolysate solution was filtered, and extracted, with 1:1 (v:v) acetone: benzene by a separatory partioning technique. The benzene layer was washed with deionized water to remove traces of acetone. Benzene was then reduced in volume and subsequently screened for hydrocarbons, and sulfur containing hydrocarbons by gas chromatography utilizing flame ionization and flame photometric detectors, respectively.

Filtered residues were analyzed for total sulfur using the LECO induction furnace to convert sulfur to SO_2 followed by idometric filtration of the SO_2.

A study was conducted to determine H_2S emissions as a function of time, pH and mix design at 185°F (85°C). This temperature corresponds to the maximum surface temperature measured for asphalt, and sulfur asphalt mats exposed to the elements in the volatilization study. The time factor was evaluated in ten minute intervals once the test temperature was attained. Results are summarized in Table 29 and 30. An

Table 29. H_2S Emissions as a Function of Mix Design, pH and Time.

Solution pH	Time[1] (Min.)	Mix Design[2] 1	2	3	4	5	6
				ppm H_2S[3]			
2.45	t_o	0.2	1.7	0.1	0.2	1.0	0.0
2.45	t_{10}	0.4	1.8	0.1	0.4	1.0	0.1
2.45	t_{20}	0.4	2.1	0.2	0.5	1.3	0.1
2.45	t30	0.3	1.4	0.2	0.5	1.5	0.1
10.7	t_o	4.4	2.7	8.7	0.7	5.5	0.2
10.7	t_{10}	4.2	3.0	9.6	1.2	6.1	0.4
10.7	t_{20}	4.0	3.2	9.4	1.1	5.7	0.4
10.7	t_{30}	4.1	2.2	8.9	1.0	6.0	0.7

[1] t_o taken at point where vapor T = 85°C

[2] Average of two determinations.

[3] For mix design details see progress report No. 6.

Table 30. ANOVA for H_2S as a Function of Mix Design, pH and Time at 185°F (85°C)

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Exponent F
pH	1	249.94	249.94	614**
Mix Design (MD)	5	222.29	44.46	109**
time (t)	3	1.10	0.37	0.91
pH x MD	5	224.4	44.88	110**
pH x t	3	0.44	0.14	0.36
MD x t	15	2.33	0.14	0.37
pH x MD x t	15	0.81	0.05	0.13
Error	48	19.51	0.41	
Total	95	720.72		

** Significant at the 1% level.

analysis of variance (ANOVA) revealed that mix design and pH had a highly significant affect on the H_2S measured, as shown in Table 30. Time of measurement was not a significant factor. A highly significant interaction occurred between pH and mix design, suggesting a neutralization reaction of the acidic media with the limestone aggregate. Equilibrium pH measurements on the hydrolysates support this premise. Mix Design 4, hydrolyzed in pH 2.45 acid solution, reacted to give an equilibrium pH of 7.55. Hydrolysis in a pH 10.7 base resulted in a hydrolysate pH of 8.7. There was very little difference in H_2S emission for MD-4 at 185°F (85°C) with respect to pH of hydrolyzing solution. This is shown in Table 31 with its associated ANOVA given in Table 32. Conversely a significant difference results in H_2S emissions for MD-3 between pH 2.45 and 10.7. Equilibrium pH values were 2.7 and 7.1, following hydrolysis in pH 2.45 and pH 10.7 solutions, respectively.

These data suggest that hydrolysis reactions may have some long term affect on sulfur-asphalt pavement. However, the effect tends to be mitigated by the aggregate system such that one would not expect environmentally significant quantities of sulfur emanating from sulfur-asphalt via chemical hydrolysis.

Analysis of hydrolysates by gas chromatographic techniques revealed that no organics were solubilized by hydrolysis reactions in either pH 2.45 or pH 10.7 water at a reaction temperature equivalent to the maximum surface temperature. Much more acidic or basic reactions, at the pavement surface, than could occur naturally would be required to induce chemical hydrolysis of sulfur asphalt pavements.

Total sulfur analysis of pavement residues, following the filtration of hydrolysates, revealed that all of the sulfur for the various mix designs was recovered in the residues. Statistically comparing mean values for percent total sulfur in the mix designs with corresponding values determined for the residues following hydrolysis using a paired t-test revealed no difference in the means. This suggests that

Table 31. H_2S Emissions as a Function of Mix Designs and pH.

Solution pH	Mix Design* 1	2	3	4	5	6
	H_2S ppm					
2.45	0.3	1.7	0.4	0.4	1.4	0.1
5.98	1.4	1.4	2.6	0.6	3.3	0.2
10.70	4.0	3.1	10.6	1.1	7.5	0.6

* Average of two determinations.

Table 32. ANOVA for H_2S as a Function of Mix Design and pH.

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	Exponent F
Between pH	2	110.44	55.22	448**
Between Mix Design	5	93.76	18.75	152**
Interaction	10	82.69	8.27	67**
Error	18	2.22	0.12	
Total	35	289.12		

** Significant at the 1% level.

the H_2S lost during hydrolysis was too low in magnitude to materially affect the total sulfur composition of the mix designs during the reaction time interval employed in this experiment.

3.1.3. 3 Biological Weathering

The various mix designs were ground to pass a 1 mm mesh sieve and incorporated into a 100 g fresh soil matrix to determine potential biological degradation. Degradation was followed by CO_2 evolution over a 90 day incubation period.

Soil was maintained at a field capacity moisuture level throughout the experiment. Field capacity is considered an optimum moisture level for soil microbial activity. The soil employed for this test was a sandy loam, which has a high native fertility, although low in nitrogen. No nitrogen was added in this study to better simulate natural conditions.

Biological degradation estimated as cumulative CO_2 evolved is given for the various mix designs in Table 33. The data suggest that sulfur tends to increase the biological activity of the soil. It should be noted that the material may behave quite differently had nitrogen been added to the system.

Although the experimental design tends to maximize the effects of biological degradation, it is certainly a plausible mechanism which will need further study at a field level. There are micro-organisms common to all soils which can utilize sulfur as an energy source. It is suggested from these data that soil microbes may be extremely important in the overall long term weathering of sulfur asphalt paving materials.

Weathering of in-service pavements by naturally occurring conditions should have no measurable impact on the environment, as assessed by simulated laboratory and relatively short term outdoor exposure studies.

Table 33. CO_2 Evolved from Asphalt, Sulfur/Asphalt and Sulfur Concrete Materials Incorporated into a Soil Matrix.

Mix Design	Cumulative CO_2 Evolved
	Mg
MD-1	194
MD-2	171
MD-3	149
MD-4	311
MD-5	373
MD-6	105
MD-7	136
MD-9	366
Soil Blank	183

3.1.4. Simulated Fire Tests

A number of samples approximately 3 x 4 x 1/2-inch thick (75 x 100 x 13 mm) were prepared from all of the sulfur mixtures for flamability tests in accordance with ASTM-D1692. Test specimens of sulfur, sulfur concrete, sulfur with DCPD, sulfur concrete with DCPD, sand-asphalt-sulfur and sulfur extended asphalt were exposed directly to a flame for a period of sixty seconds after which the flame was removed. While in contact with the flame, the sulfur and the sulfur concrete tended to melt, with only the foamed residue (intumescence) burning. Both samples, however, self extinguished when the flame was removed. The sulfur with DCPD also melted but the intumescent material burned more readily and continued to burn until the sample was totally consumed. The sand-asphalt-sulfur and sulfur extended asphalt samples burned with the evolution of a considerable amount of black smoke while in contact with the flame from the burner. When the flame was removed the smoke was reduced after about 6 seconds and both materials self extinguished. As expected, H_2S and SO_2 gases were emitted to a level beyond the range of the monitoring instruments (100 ppm) while maintaining direct flame contact, but reduced to trace levels within 10 seconds after the flame was removed and the temperature of the surface cooled.

A sample of asphalt cement was also exposed to direct flame. The sample did ignite and continued to smolder until the ash was created. The black smoke was generated in the asphalt samples but not in the pure sulfur sample. Only the sulfur containing samples emitted H_2S and SO_2. It was noticed that the presence of aggregate slowed the burning, and in all but the sulfur concrete with DCPD actually created a self extinguishing element.

It was concluded that barring any direct flame contact with a sulfur-asphalt or sulfur concrete, the surface would not readily ignite. Except for the DCPD sulfur concrete, none of the systems tested sustained a burn once the burner flame was removed. However, assuming ignition did take place the burning surface would self extinguish with only local environmental impact. Treatment of sulfur fires is discussed in the Field Evaluation Plan - Volume II.

Compacted specimens were also subjected to another laboratory simulated fire test using the controlled environment set-up given in Figure 29. It became clear on the initial test that the Interscan gas monitors were inadequate to measure the levels of H_2S and SO_2 emitted. Therefore the concentrations of these gases were monitored using a commercially available Drager appartus. A natural gas flame was used, and the flame tip placed on the specimen throughout each trial.

Organics were trapped in refrigerated hexane using a minumum 2 trap series. Contents of both traps were combined, dried over anhydrous Na_2SO_4, and reduced in volume by vacuum distillation prior to FID and FPD gas chromatographic analyses.

Compacted specimens resulted in a much different distribution of inorganic sulfur than anticipated, particularly with respect to the H_2S and SO_2 levels (Table 34). Neither H_2S and SO_2 were detected by Drager tube analysis of the asphalt control material (MD-6). Both sulfur concrete MD-8 and 9 produced extremely high concentrations of SO_2 relative to the sulfur-asphalt systems. H_2S was generated in the DCPD-modified material but not in the unmodified sulfur concrete.

Table 34. H_2S and SO_2 Concentrations Emitted during a Simulated Burn.

Sulfur Specie	Mix Design								
	1	2	3	4	5	6	7	8	9
	Concentration, ppm								
H_2S	25	18	350	75	25	0]	20	0	25
SO_2	100	47	750	65	25	0	30	2800	3400

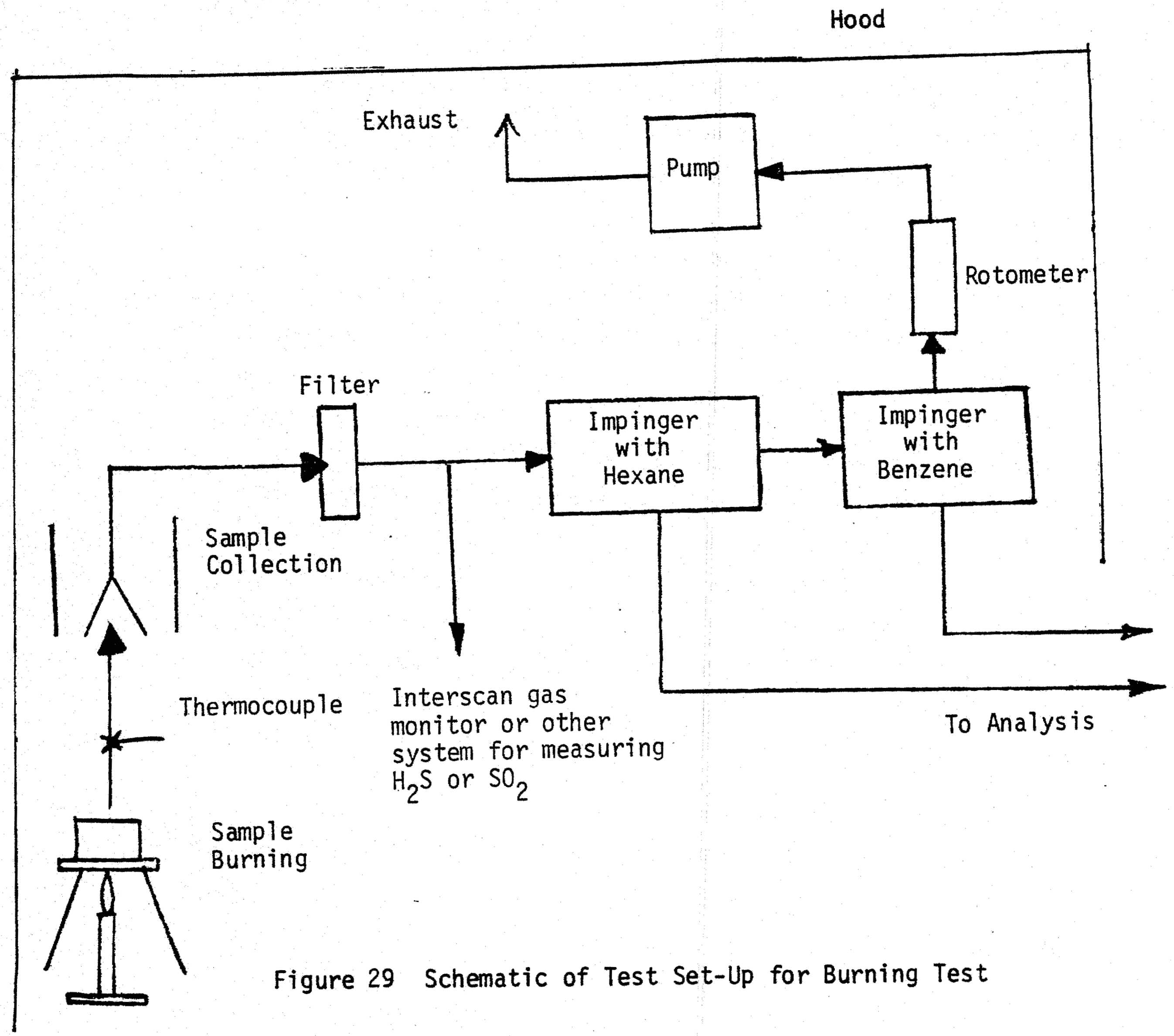


Figure 29 Schematic of Test Set-Up for Burning Test

Sulfur-asphalt materials, with the exception of the MD-3 design resulted in surprisingly low gaseous sulfur values, but with proportionally higher H_2S levels than anticipated. The high sulfur containing pavement (MD-3) and the sulfur concrete speciemsn (MD-8 and MD-9) yielded much higher SO_2 levels, with only MD-3 resulting in a significant H_2S level. The asphalt matrix definitely reduced sulfur emissions.

Attempts to recover particulate sulfur were completely frustrated due to immediate deposition on cooler surfaces of the apparatus glassware. Therefore a material sulfur balance was not attempted.

Although it was impossible to quantitate total organic emissions, FID scans revealed significant emissions for the sulfur asphalt pavements. Comparison of organic emissions trapped for MD-3 and MD-6 suggested that elemental sulfur mixed with asphalt does not materially affect the nature of the organics released on burning (Figure 30). Sulfur alone dominated the FPD scans, and is demonstrated in Figure 31, for a 1 to 10 dilution MD-3.

Although dense fumes were noticeable throughout the test, low levels of organics actually trapped in refrigerated solvent indicated an inadequate design of the test procedure. However, attempts to modify the system were completely thwarted by the physical nature of the fumes. Apparently the organics emitted were occluded with or onto sulfur particulates.

3.1.5 Simulated Spills

Compacted specimens of the asphalt and sulfur paving materials (Mix Designs 1 through 7) were fragmented into particles retained on a 2 mm sieve. Ten gram samples of each material were then placed in glass columns and leached with 100 ml saturaged NaCl at an elution rate of 4 ml per minute. Leachates were acidified to pH 6 and extracted by a separating funnel partition technique into benzene using 2.50 ml volumes of the latter. Benzene extracts were combined, dried over anhydrous Na_2SO_4, reduced in volume and subsequently analyzed by gas chromatography using both FID and FPD detector systems.

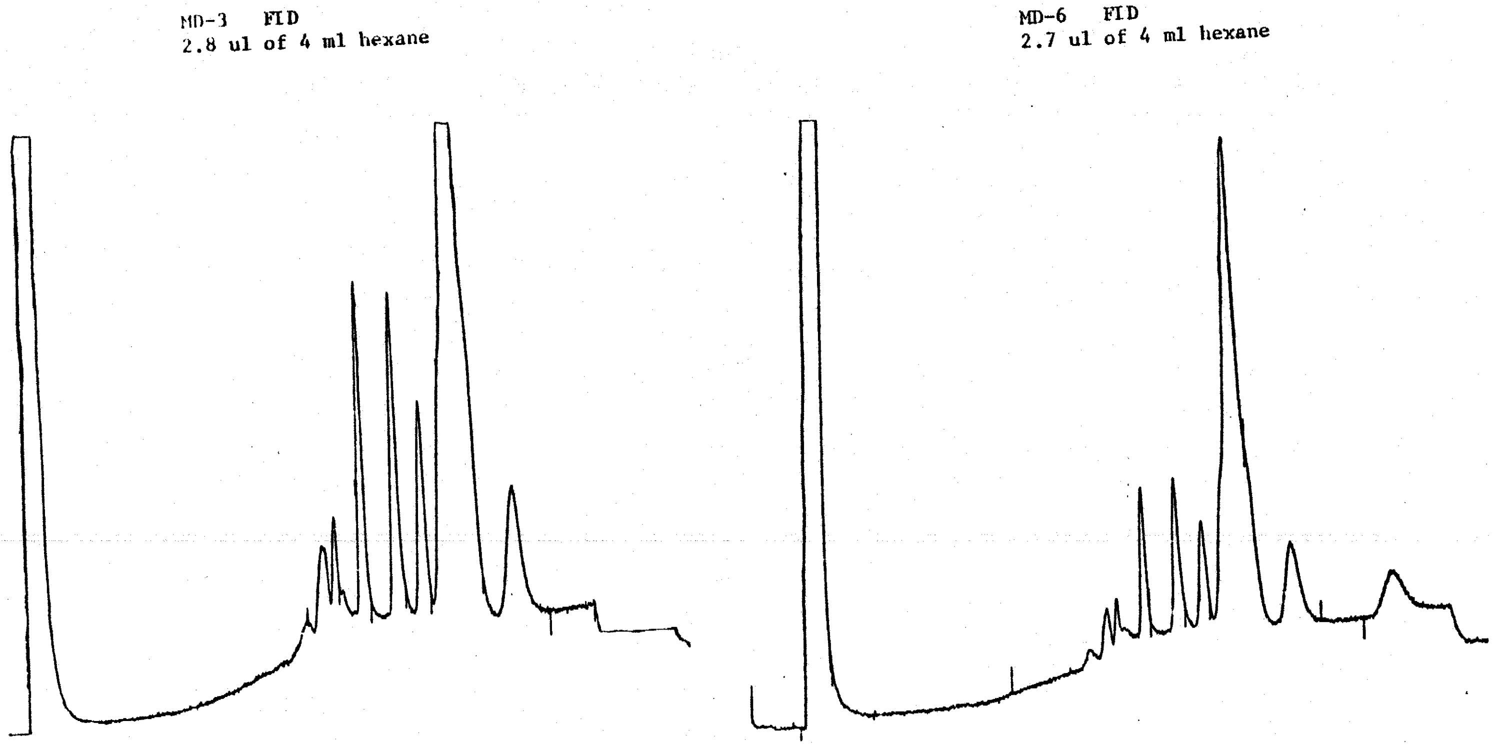


Figure 30. FID Scans of Emissions Generated on Burning Compacted Specimens of MD-3 and MD-6.

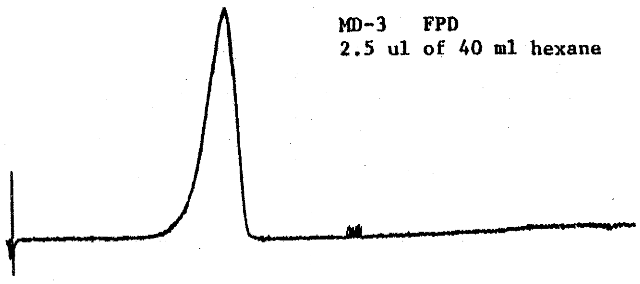


Figure 31. FPD Scan of Emissions Generated on Burning a Compacted Specimens of MD-3.

A separate 10g subsamples was leached with a 100 ml volume of nanograde quality iso-octane. Iso-octane extracts were simply dried over anhydrous Na_2SO_4 and analyzed by gas chromatography using both FID and FPD detector systems.

Saturated NaCl leach solution was used to simulate the affect of potential brines from deicing salts on sulfur-asphalt paving materials. FID scans of leachates (Figure 32) generated showed absolutely no organics were stripped from either asphalt or sulfur-asphalt materials with the column leach technique employed. The peaks showing up in several of the scans were found to be contaminates of the Na_2SO_4 used to dry the benzene extract. The elemental sulfur blank is designated as such. Straight line chromatograms were obtained in the FPD mode on analyses of the brine leach for sulfur containing components. The use of fractured pavement specimens in the test gave a much larger surface area than an intact pavement, and maximize the effectiveness of the brine leach on a comparative basis. One can only conclude from these results that brine of saturated deicing salts would have a minimal impact on run-off waters emanating from sulfur-asphalt or asphalt pavements.

Simulated gasoline spills, using iso-octane as a leach solvent, revealed that this may leach elemental sulfur from contacted surface materials (Figure 33 through 40). This is based on the fact that sulfur shows up on FPD detection with no commensurate peak in the FID model. The impact of a gasoline spill will of course be lessened with an intact compacted pavement surface. However, the fact remains that organic solvents or naptha mixtures will solubilize free sulfur.

The data suggests that a much longer contact time than that afforded by the column leach technique employed would be required to solubilize significant asphalt borne organics.

3.1.6 Effect of Dicyclopentadiene (DCPD) on H_2S and SO_2 Emissions From Sulfur Concrete Mixes

Dicyclopentadiene (DCPD) is one of the primary additives currently being used to plastize sulfur for use as a binder in sulfur concretes. The examination of gas evolution associated with the presence of DCPD in the system should be considered from

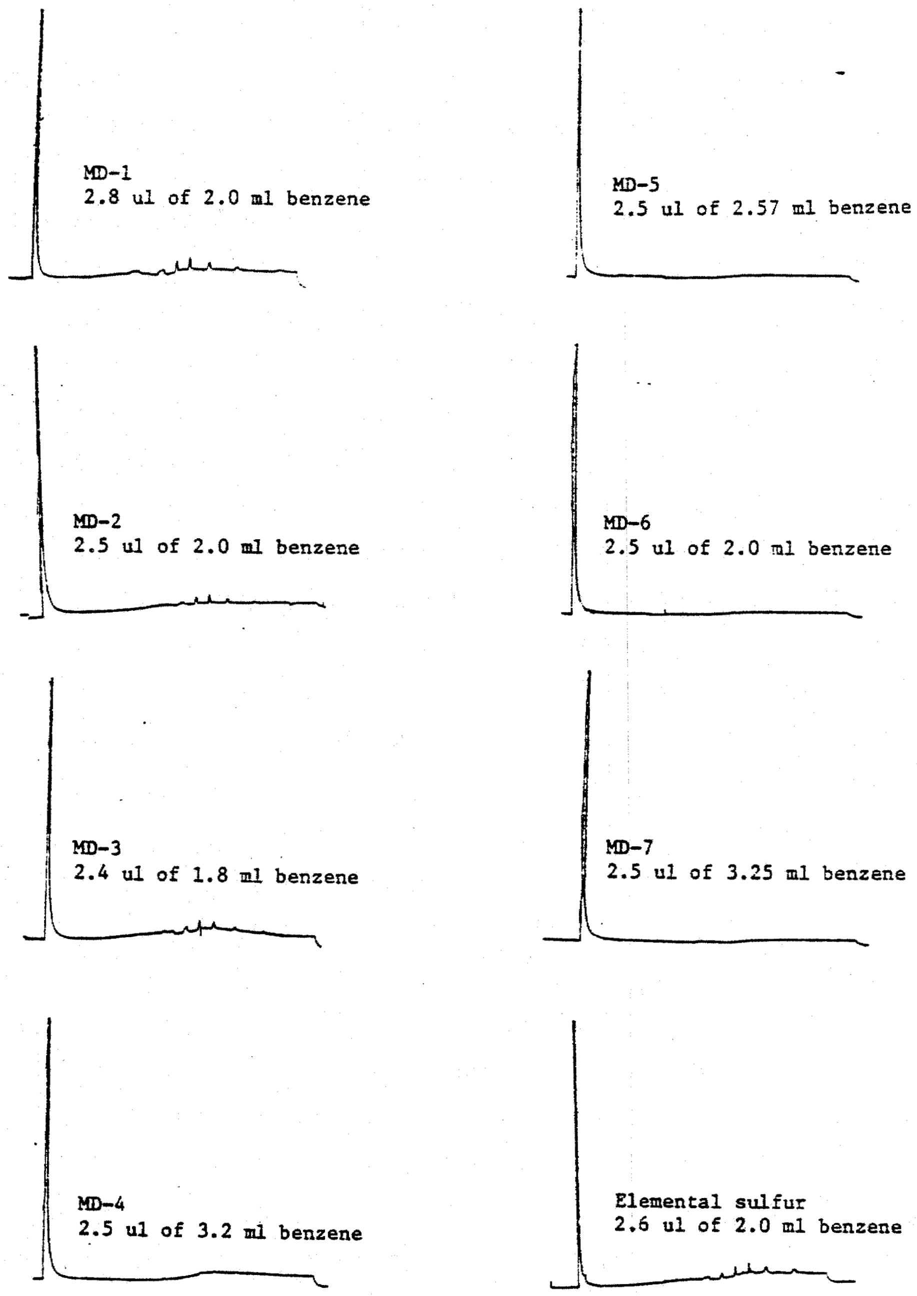


Figure 32. FID Scans of Fragmented Paving Materials Leached with Saturated NaCl.

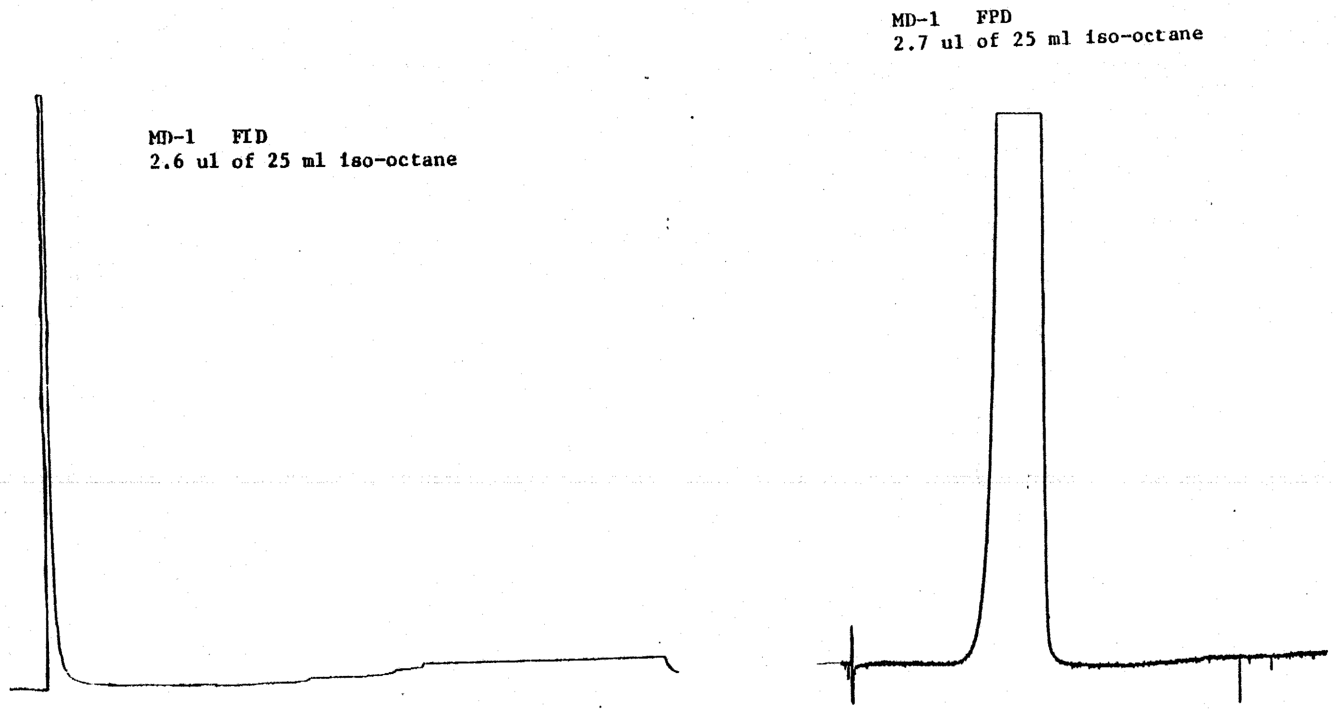


Figure 33. FID and FPD Scans of Fragmented MD-1 Paving Material Leached with Iso-Octane.

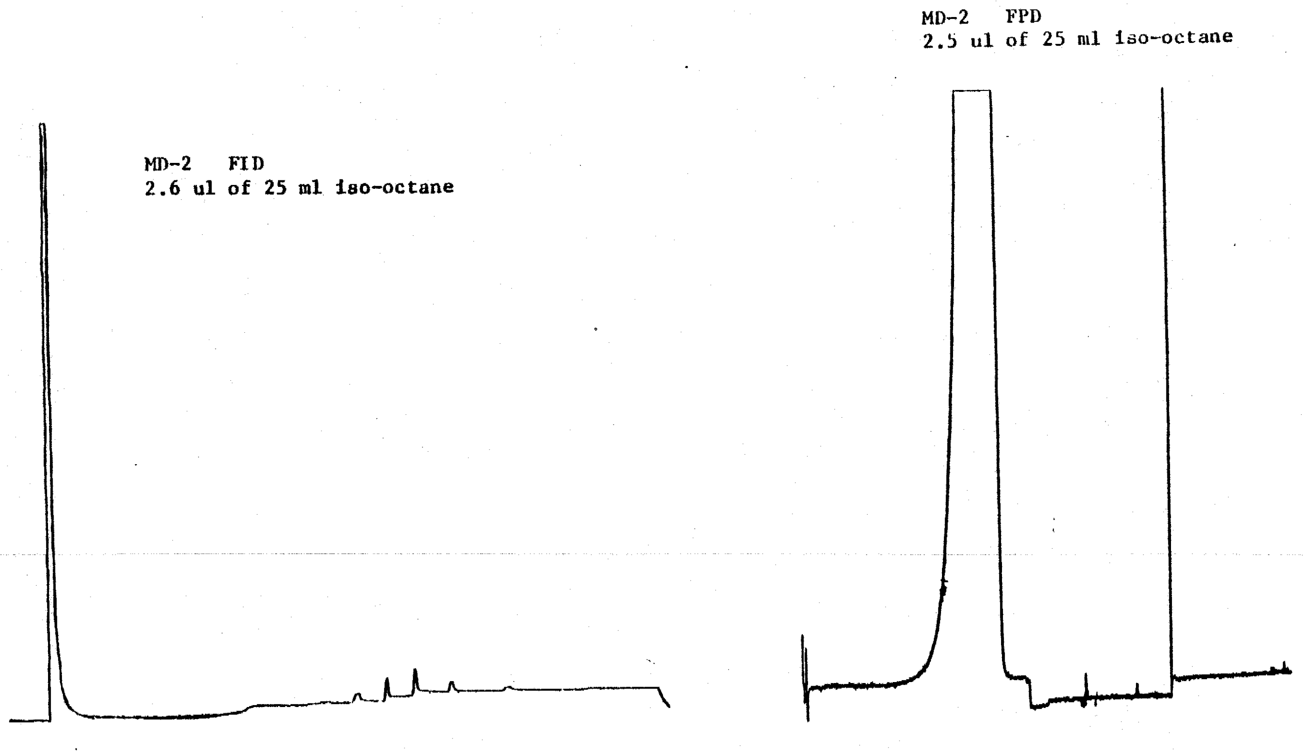


Figure 34. FID and FPD Scans of Fragmented MD-2 Paving Material Leached with Iso-Octane.

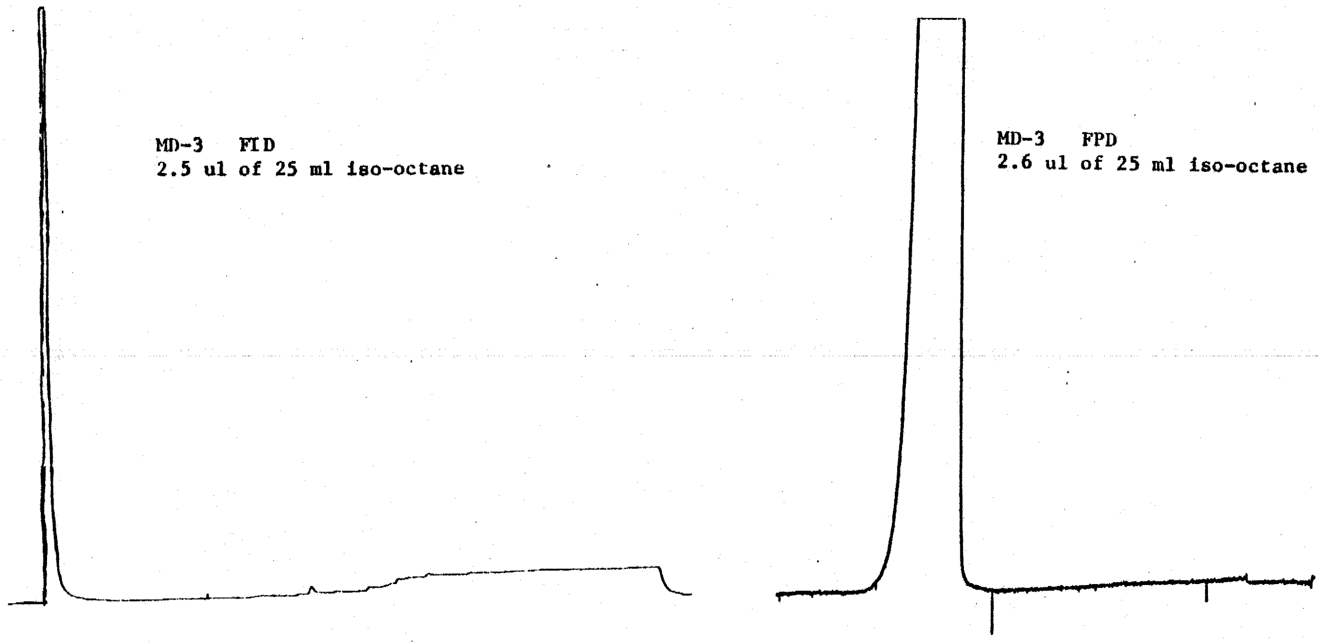


Figure 35. FID and FPD Scans of Fragmented MD-3 Paving Material Leached with Iso-Octane.

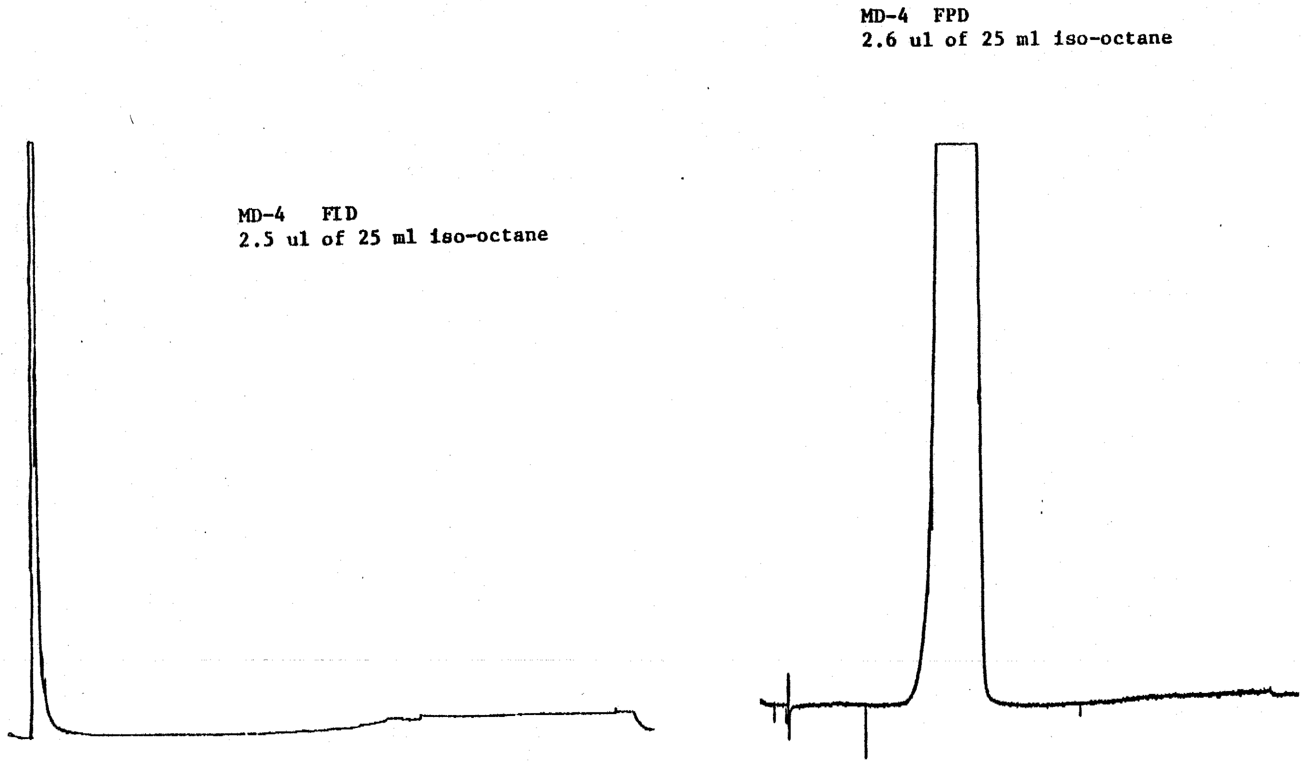


Figure 36. FID and FPD Scans of Fragmented MD-4 Paving Material Leached with Iso-Octane.

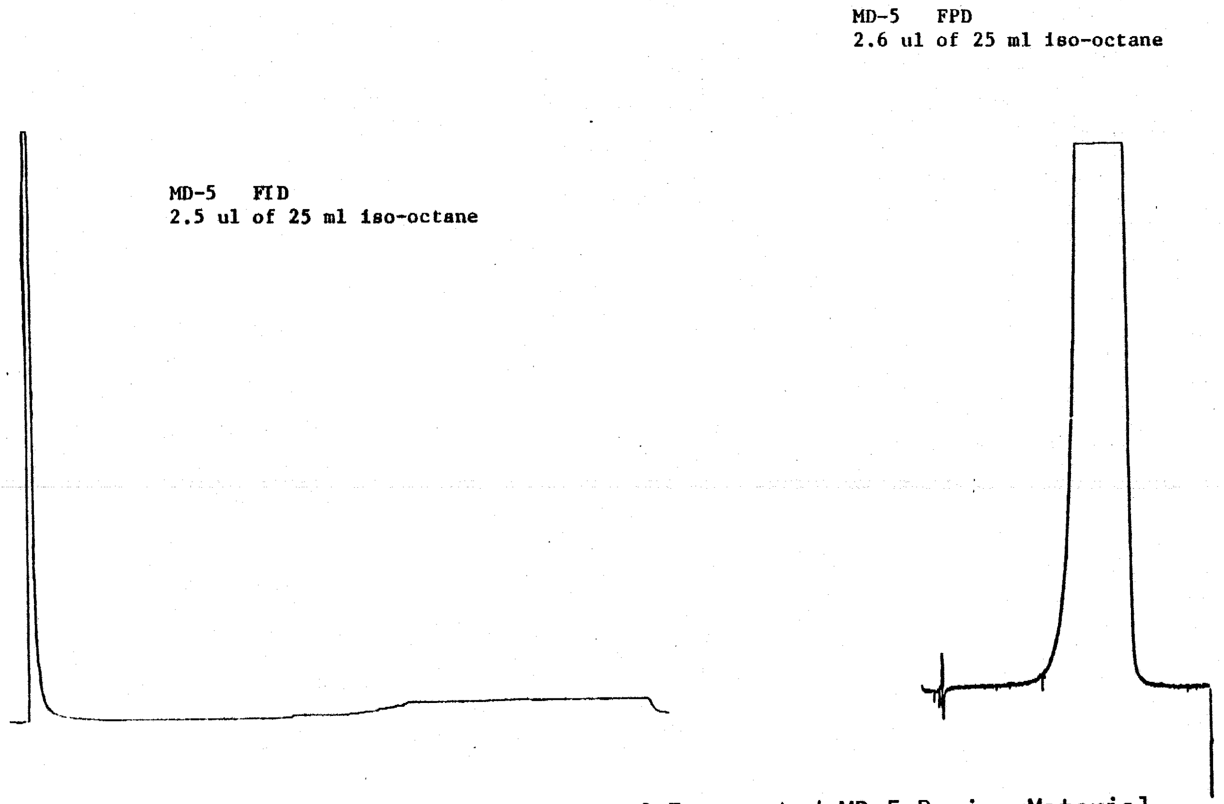


Figure 37. FID and FPD Scans of Fragmented MD-5 Paving Material Leached with Iso-Octane.

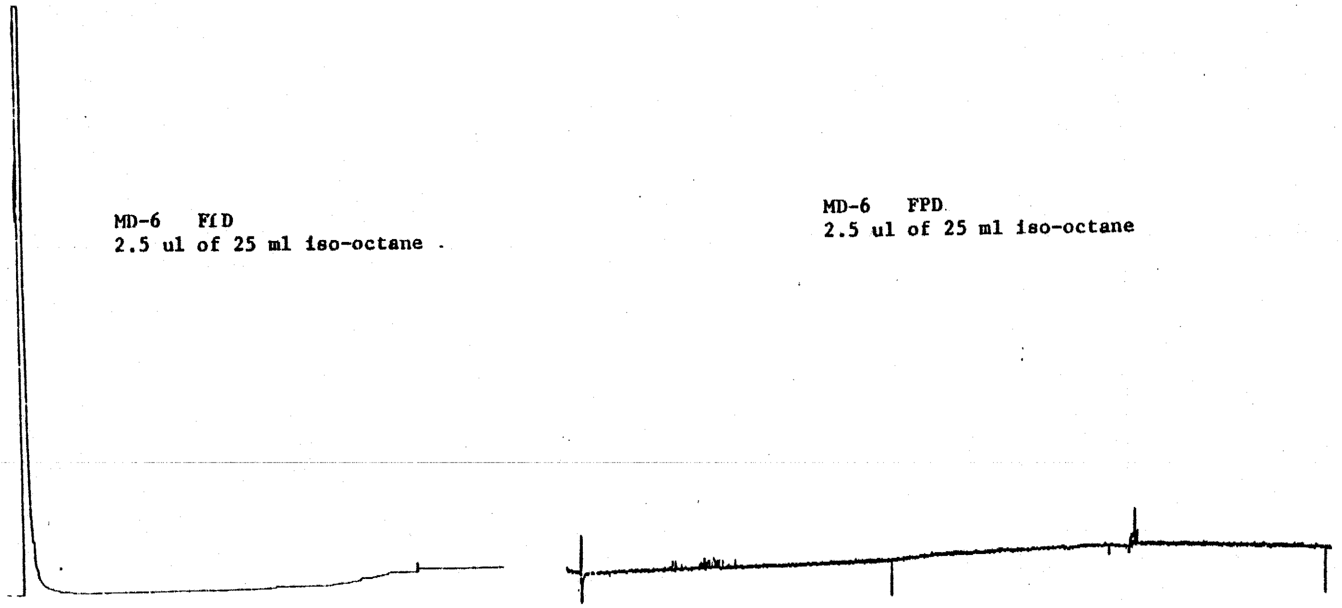


Figure 38. FID and FPD Scans of Fragmented MD-6 Paving Material Leached with Iso-Octane.

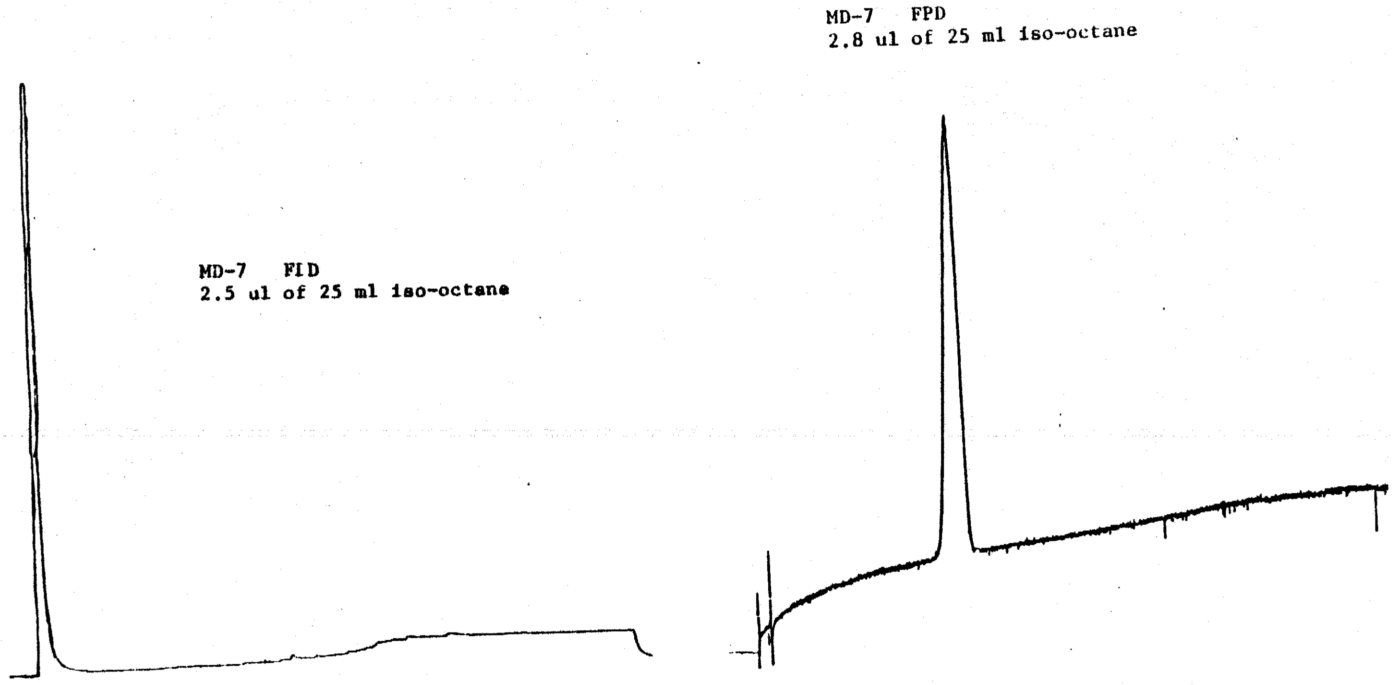


Figure 39. FID and FPD Scans of Fragmented MD-7 Paving Materials Leached with Iso-Octane.

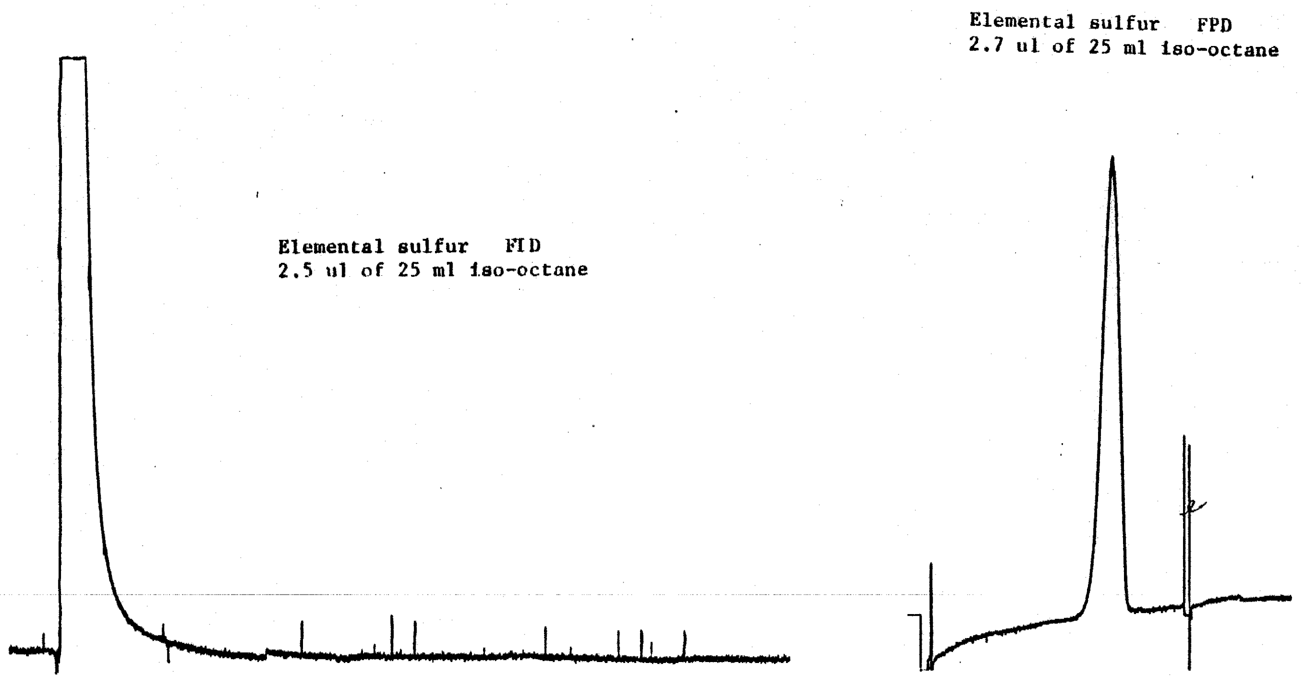


Figure 40. FID and FPD Scan of Fragmented Elemental Sulfur Leached with Iso-Octane.

two aspects; binder preparation and concrete production. In the former, the DCPD-sulfur reaction is of prime importance whereas in the latter the exposure of the binder to mixing temperatures of 250 to 350°F (121 to 177°C) is the main concern.

At the reaction temperature necessary for polymerization with sulfur 250 to 285°F (121 to 141°C), DCPD immediately depolymerizes to the cyclopentadiene (CPD) producing a highly exothermic reaction. If the exotherm is permitted to occur, the sulfur temperature can be raised to levels which may produce high levels of H_2S and SO_2. One way of controlling this reaction is to introduce the DCPD at a relatively slow rate or by premixing the DCPD and sulfur at room temperature prior to heating [19]. Another approach developed by The Bureau of Mines [20] utilizes a preblend of DCPD and its oligomer to slow down the reaction with sulfur and significantly reduce the exotherm. An in depth FHWA-sponsored research study [44] is looking into, not only H_2S and SO_2 generation, but other potentially hazardous pollutants which may be produced under the conditions that plasticized sulfur binders are processed. Therefore, the binder preparation aspect was not treated in this report.

This phase of the program dealt primarily with assessing the H_2S and SO_2 emissions generated during a typical sulfur concrete mixing operation. This was accomplished by monitoring the air space in the laboratory approximately 18 in (46 cm) over the mixing bowls using the H_2S and SO_2 Interscan monitors. Peak emissions from a DCPD-modified sulfur concrete mix (MD-9) were compared with the unmodified sulfur concrete (MD-8). The mixes were prepared at three temperatures; 250°F (121°C), 300°F (149°C) and 350°F (177°C). Total mixing time for each material never exceeded one minute. The peak dissipated after 15 seconds. The H_2S and SO_2 concentration, as measured, are shown in Table 35.

Table 35. Variation of H_2S and SO_2 Emissions with Mix Temperature Generated during Sulfur Concrete Mixing - Laboratory Environment

Gas		Temperature °F (°C)	Mix Design*	
			8	9
H_2S	5 sec.	250 (121)	Tr	1.0
	(15 sec.)		(0)	(Tr)
		300 (149)	0.8	1.1
			(Tr)	(Tr)
		350 (176)	23.1	31.2
			2.8	3.0
SO_2	5 sec.	250 (121)	Tr	Tr
	(15 sec.)		(0)	(0)
		300 (149)	Tr	1.0
			(0)	(Tr)
		350 (176)	16.8	22.3
			3.1	4.1

*Mix designs are given in Table 11, page 39

Consistent with that found for the sulfur-asphalt systems (see Table 13b), H_2S and SO_2 emissions remain at safe levels up to 300°F (149°F). Although the MAC values were exceeded for both MD-8 and MD-9 at the 350°F (177°C) temperature, they were rapidly diminished after 15 seconds of mixing. Where detectable, emissions from MD-9 were slightly higher than those generated in MD-8. It should be noted that at all temperatures, rather obnoxious odors were present during mixing which could prove objectionable to personnel. It is therefore recommended that sulfur concrete mixing be carried out at temperatures no greater than 300°F (149°C) and in well ventilated areas.

3.2 Task B - Human Safety and Environmental Aspects

3.2.1 Human Safety and Hazard Considerations

The results generated in Task A continue to support the fact that as long as sulfur-asphalt or sulfur concrete mixtures are maintained at temperatures which do not exceed 300°F (149°C) problems associated with the evolution of toxic pollutants are minimal. A more detailed treatment of the nature of the hazards and safety practices recommended for construction personnel is given in Volume II of this report.

The primary contaminants to which workers could be exposed in measurable amounts during production, placement and post construction maintenance of sulfur modified paving materials include Hydrogen Sulfide (H_2S), Sulfur Dioxide (SO_2), Sulfur Trioxide (SO_3) and particulate (elemental) sulfur. Each of these pollutants is capable of causing acute illness if the concentrations at which they exist exceed their respective Maximum Allowable Concentration (MAC) threshold. The relative toxity levels of H_2S, SO_2 and particulate sulfur have already been discussed in Section 1.1.4.

Results of Task A indicate that under normal recommended operating conditions it is unlikely that conditions could occur that would produce hazardous concentrations of SO_3 and subsequent illness. On the other hand, conditions could occur which could produce toxic levels of H_2S and SO_2. These include:

(a) Storage of hot sulfur-asphalt mixture in enclosed, poorly vented containers such as storage silos. Storage time of hot sulfur-asphalt mixes should be limited to a maximum of 4 hours. Overnight silo storage is not advised.

(b) Sulfur storage tanks can accumulate H_2S and SO_2 at concentrations well above the lethal level, and personnel working around open ports or sulfur discharge values for prolonged time periods should be equipped with a respirator.

(c) Pug Mill hoppers or feeds require periodic inspection for material "hang up" or clogging. Visual inspection by plant personnel is usually accomplished by climbing stairs or ladders to look inside the hoppers. Under certain atmospheric conditions, toxic fumes can accumulate to levels which may be hazardous to the workman.

Particulate sulfur can be generated during mixing, dumping into trucks under the pug mill, dumping into the paver hopper or the mixing action of the paver screw. Sulfur particles are carried into the air in a vapor wherein they cool and become fine sulfur dust. Except for the eyes, skin or mucosa, irritation is short term and can be prevented by wearing goggles and/or masks. Irritation is usually relieved by washing with water. Clothing requirements for personnel who must work with hot, liquid sulfur are the same as for asphalt and is discussed in Volume II of this report.

Aside from eye or skin irritation, temporary discomfort can arise from odor. The extent of this discomfort is subjective and dependent on the specific sensitivity of each other. It is noteworthy that in communications with sulfur producers (e.g., Texas Gulf in Texas) records show that virtually no immediate or chronic illness related directly to sulfur has developed at their facility during the past 50 years.

Of the contaminants of interest, only SO_2, SO_3, and H_2S are suspected of causing chronic illness. Chronic illness due to exposure to SO_2, H_2S, or SO_3 is not expected based on the curent information available on these compounds and Task A. These results indicate that all exposures are anticipated to be at levels considerably below the maximum allowable concentration (MAC) considered acceptable for continuous exposure during an 8 hour working day.

Although sulfur-asphalt is combustible, the fire hazard associated with it is minimal. Liquid sulfur, sulfur vapor, and sulfur dust all are combustible, and fires can not be totally ignored. Although the likelihood of conditions suitable for a sulfur dust explosion is very slight this possibility should be recognized. Establishment procedures for the safe handling of liquid sulfur being used in that industry will minimize the fire and explosion hazard.

At the mix temperatures expected, asphalt will have only a minimal fire hazard associated with it. Correct safety and handling procedures are already known in the paving industry and are recommended for use on sulfur-asphalt systems, as well.

Under very extreme conditions, enclosed storage at excessive temperatures, it is theoretically possible that sufficient H_2S could be generated to form explosive mixtures with air. With adequate temperatures control, it seems very unlikely that this will occur in practice, however, all the materials involved in producing sulfur asphalt paving mixtures are heated to temperatures capable of producing a skin burn. Molten sulfur is a special problem, as improper handling could significantly increase the chances of personnel being burned.

Exposure limits for all the identified contaminants have been set by the American Conference of Governmental Industrial Hygienists (ACGIH) as threshold limit values (TLV's) and by OSHA as maximum allowable concentrations (MAC). In both cases the values for eight hours -- time weighted average (TWA) exposure are:

Contaminant	TLV
H_2S	10 ppm
SO_2	5 ppm
particulate sulfur	10 mg/m^3
asphalt fumes	2 mg/m^3
SO_3	2 mg/m^3

Although 10 ppm has been set as the TLV for H_2S by the ACGIH, the upper limit established for all of TTI's sulfur field trials programs has been set at 5 ppm.

3.2.2 Short Term Environmental Effects on Soils, Flora and Fauna

A shortage of sulfur-containing amino acids is one of the worlds most pressing problems with respect to human nutrition. Paradoxically, urban pollution is one of the most important sources of sulfur. Recent measures taken to reduce pollution have materially reduced this sulfur supply and rendered more and more soils to a sulfur deficient status. As sulfur enters the terrestrial environment, less oxidized forms will be converted to sulfates within the chemically and biologically active surface volume of aerated soils. Agronomically important soils have little capacity to absorb anions and SO_4 produced tends to be leached from the system. Acid soils tend to have adequate sulfur supplies fixed as precipitated metal sulfates. Weathered soils in humid moisture regimes are generally dependent upon sulfur containing fertilizers and sulfur pollutants to sustain supplies essential for plant growth.

It has been established that the bulk of sulfur released from the construction of sulfur-asphalt pavement materials, is inorganic sulfur. Principally the sulfur is in a free elemental form. Temperatures above 300°F (149°C) favor the formation of both H_2S and SO_2, which may exceed 500 ppm in a closed environment, such as that incurred during formulation, storage and transport. The potential hazards to human health and safety are addressed in Volume II.

The release of inorganic sulfur into the environment is most likely to occur during the paving process. Elemental sulfur released initially in a vaporous state will be rapidly cooled and condense to fine particulates. Elemental sulfur, due to its mass, will only be transported short distances via wind currents. H_2S and SO_2 released during the paving process can be transported relatively long distances since both are gases. The environmental impact of these gases are attenuated by distance transported via a dilution mechanism.

Elemental sulfur is not readily altered chemically due to insolubility in water. Elemental sulfur and its sulfides serve as electron donors for aerobic or anaerobic respiration by soil microflora with the formation of sulfates [45, 46]. Extremely acidic conditions accompany the oxidation of these reduced species, which can impart an adverse impact if the soil does not have sufficient neutralizing capacity to buffer the acidity produced. For weathered soils with insufficient buffer capacity the impact may induce aluminum and manganese concentrations toxic to sensitive agronomic crops. Soils of sufficient buffer capacity will in most cases benefit from the sulfur added. Marginal soils and those of insufficient buffer capacity can be limed by an inexpensive broadcast application to neutralize the acidity produced on oxidation of reduced sulfur.

Soils readily absorb H_2S and SO_2 gases [47, 48]. The absorption process is independent of microflora activity in soils. It had been demonstrated that SO_2 is chemically oxidized to SO_4. The reaction is not as acidifying as oxidation of the more reduced species.

The greatest potential for an adverse impact arising from sulfur-asphalt materials is from SO_2 generated during with mixing and paving process. Many oranamentals and agronomic plant species are adversely affected by relatively low concentrations of SO_2 [49-54]. However, the fact that the SO_2 generated will be rapidly dissipated and of short duration, grater reduces the potential for permanent plant damage [55]. Timing for a paving operation can also be used to lessen the potential for an adverse impact where sensitive plant species are in close proximity to the road bed. Research has shown that plants are more likely to be injured by low levels of SO_2 at high temperatures and high relative humidities [51, 56]. H_2S at the concentrations potentially emitted during the paving operation will have no adverse impact on plant communities. It has been suggested that low levels of H_2S may even be beneficial to agronomic crops [52].

Sulfur-asphalt pavements once constructed will have little impact on the environment. Gasoline spills may strip some sulfur as it runs off the pavement, but will rapidly penetrate soils such that only the road bed and adjacent soil zone would be affected. Liming materials used in the construction of road beds will more than neutralize potential acidity produced once in soil contact. The practice of stabilizing soils beyond the intended pavement surface will also negate potential acidity generated from sulfur dusts.

Large concentrations of SO_2 could result if a fire broke out following an accident, and cause damage to flora in the immediate area.

3.2.3 Short Term Environmental Effects on Structural Materials

Once the sulfur modified pavement is in service, the combined action of rain, wind and traffic could produce run-off or splashing that may have an effect on some of the structural materials normally found in the vicinity of a road. Under traffic wear, frictional forces between the tire and road surface will also produce a fine dust which could be transported to the side of the roady by wind or rain, or splashed onto moving or parked vehicles by back-spray from passing cars. To evaluate this effect, a number of materials were subjected to a series of tests simulating the activity just described. The materials evaluated included:

Material	Typical Location
Steel Reinforcing Rods	Sulfur Concrete Section
Galvanized Steel	Road Sign and Guard Rails
Chrome/Tin	Wheel Hubs

Material	Typical Location
Chrome Plating	Bumper
Painted Sheet Metal	Car Body and Roadway Signs
Aluminum	Nuts and Bolts, etc.
Copper	Tubing, Wiring, etc.
Rubber	Hoses, Sealants
Vinyl	Upholstery
Wood	Concrete Forms

Samples of the materials listed above were obtained from TTI's automobile "graveyard" and storage. It was decided by the project team that the test medium which would most nearly simulate the conditions described above would be a solution of finely ground paving material (i.e., minus No. 100 sieve) and water. Two particulate solutions referred to as "the leachates" were prepared using the sulfur DCPD concrete (Mix No. 102) and the sand-asphalt sulfur mix (Mix No. 3) designs. There were selected since they represented the mixes with the highest sulfur content. About 0.1 lb (45 grams) of each of the two crushed materials were added to about 1 gallon (3.8 liters) of water in a 2 ft. x 2 ft. x 1 ft. (0.51 m x 0.61 m x 0.30 m) open vessel. Three vessels were used; one for each of the two mix designs and one which contained only pure water. Samples were placed on a screen capable of being positioned so that the samples could be either totally submersed or completely above the leachate level in the vessel. The test was carried out at two temperatures; 75 and 140°F (24 and 60°C).

A sparger coil was located on the bottom of a vessel which was connected to an air supply. A control value was used to adjust air pressure to provide just enough turbulence to keep the particulate matter in suspension. The leachate was kept at a steady roll so as not to induce any abrasive action on the sample surfaces. This rolling agitation was maintained for 30 minutes after which the samples were removed from the leachate and left to dry. The test was repeated once a day for two months. After each 30 minute test, the samples were visually inspected for corrosion, chemical attack or change in surface characteristics. A schematic of the test set-up is shown in Figure 41.

Except for the copper which was chemically attacked by the sulfur-water solution, no permanent visual damage or changes were noted at either of the two test temperatures. The effect on copper was to be expected since it is an established material selection criteria not to use copper in handling or storing sulfur. The only visual effect noted was a film that formed on the painted surfaces upon drying. This was easily remedied by wiping with a clean, dry cloth.

A series of tests were also run on some steel samples in leachate solutions of varying pH. It was found that as the leachate became more acidic (i.e., pH ≤ 6) the steel samples were beginning to become pitted. At pH ≥ 7 no such activity was noted.

The results of these tests would indicate that exposure to sulfur-water solutions would be detrimental to copper and steel; the latter only in acidic solutions. This could be a problem in using reinforcing rods in moist sulfur concrete. The use of copper or copper alloys would not be advisable. Otherwise, there was no difference indicated between samples exposed to the two sulfur leachate and the pure water.

3.3 Task C - Field Evaluation Plan

The results of Tasks A and B along with pertinent information gleaned from the literature search (Task D) have been utilized to set up a detailed work plan for monitoring emissions and pollutants from operations and situations encountered in the construction and maintenance of sulfur-modified asphalt pavements. This Field Evaluation Plan in Task C of the overall project and is treated in detail in Volume II of the final report.

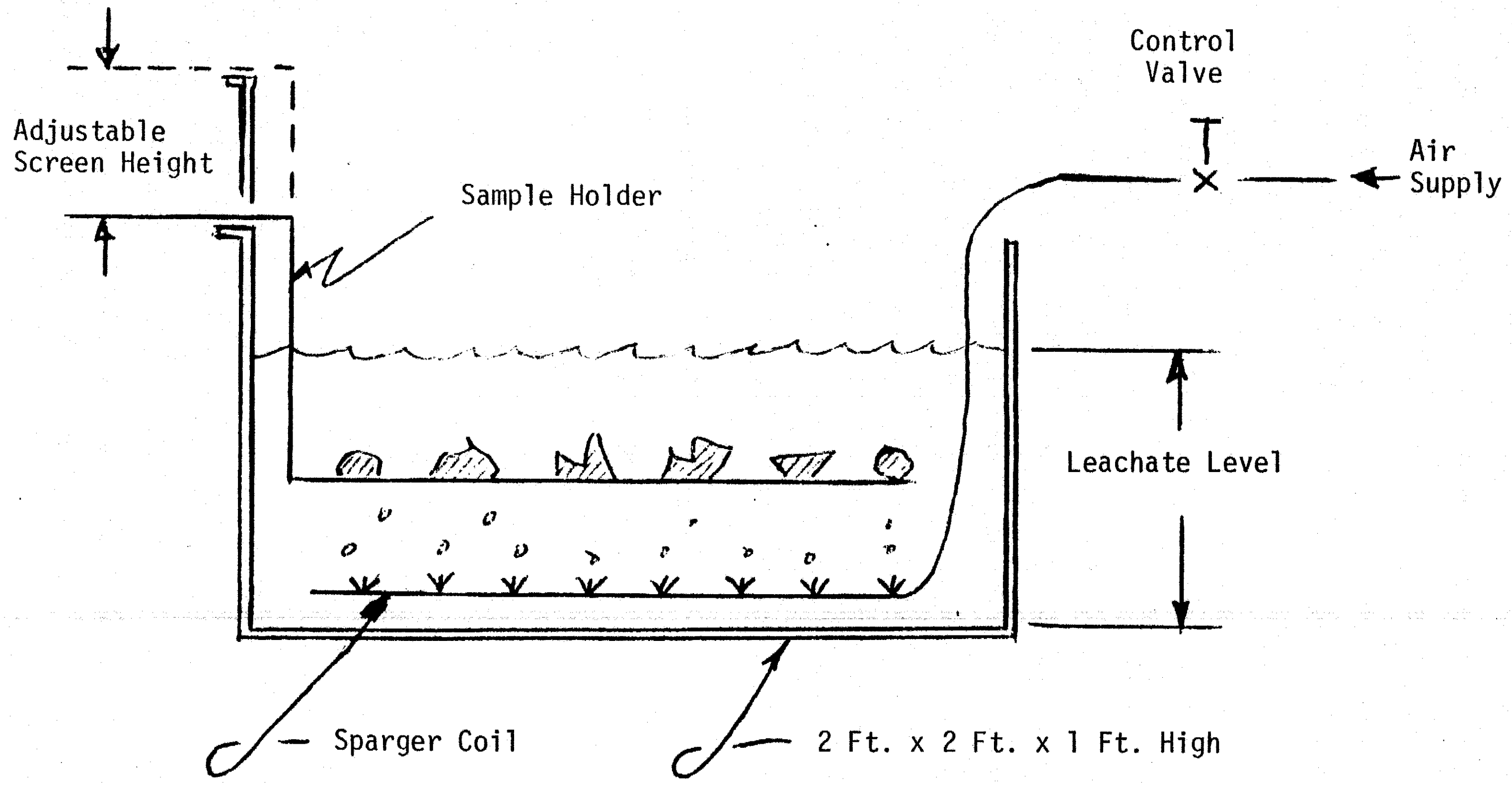


Figure 41. Schematic of Test Set-Up for Evaluating Short Term Environmental Effects on Structural Materials.

With the advent of the development of sulfur-modified asphalt pavements it has become necessary to properly evaluate the safety aspects of these materials lest the results of isolated, non-routine operating conditions misrepresent the true safety and environmental impact of this area of technology. The objective of the Field Evaluation Plan is to present a developed environmental and safety guideline for the use of sulfur in highway pavements. These guidelines include descriptions of hazards encountered in handling liquid sulfur. Symptoms of exposure to these hazards are described and first aid treatment is presented. The operations and situations encountered during construction of sulfur modified pavements are described in view of the hazards due to the presence of sulfur. Types of exposures, sources of the exposures, factors affecting the exposure levels, risk evaluation, and recommendations for appropriate safety apparel and monitoring equipment are given. The operations and situations are broken down into stationary and mobile sources of emissions and pollutants as follows:

Stationary	Qualtity Control Laboratory
	Sulfur Storage Tank
	Storage of Preblended Sulfur-Asphalt Binders
	Mixing Units
	Surge Silos
	Stacks
Mobile	Haul Trucks
	Paver

Types of maintenance operations and hot-mix recycling procedures have also been evaluated for exposure to noxious and obnoxious emissions due to the presence of sulfur in the pavement. Also included in the Field Evaluation Plan are methods of monitoring the potentially hazardous products as determined from the laboratory and simulated field tests.

Brief descriptions of some of the evolved gas analysis techniques have been presented for the types of monitoring common to the paving industry. The breakdown of emissions monitoring methods are: (1) area monitoring - continuous sampling techniques; (2) short term sampling - "grab" sampling, and (3) personnel monitoring - continuous sampling. In preparing this plan, every attempt was made to make the safety practices and working environment consistent with requirements already established by OSHA, NIOSH, and EPA in the paving and sulfur handling industries.

3.4 Task D - Annotated Bibliography

This phase of the project generated a synopsized review of the literature and appropriate patents, and provided for the establishment of a comprehensive annotated bibliography relative to the safety and environmental effects of the use of sulfur modified pavement materials. This resulting annotated bibliography is contained in Volume III of the final report for this contract and is comprised of over 500 abstracts derived from an extensive literature search. Each article has been classified into one or more of the following categories:

I. Environmental Effects
    1.0 Effects on Air and Water
    1.1 Effects on Plant Life
    1.2 Effects on Animal Life
    1.3 Bacterial - Microbiological Effects
    1.4 Effects on Soil

II. Health and Safety Aspects

III. Material and Structural Effects (Corrosive)

IV. Mechanisms and Monitoring Devices

V. Surface Abrasion and Contact of Sulfur Pavements

A suitable cross-referencing and coding system was also established. The code letters and numbers are given adjacent to each reference to indicate the particular category(s) covered in the reference.

Texas A&M University Library's Automatic Information Retrieval Service (AIRS), a computer search facility, was used to obtain over 1400 abstracts which were then reviewed, classified, and placed into the final report. The literature searched included such sources as the Chemical Abstracts, The Engineering Index, and the NTIS reports. The annotated bibliography, along with the abstractions and categorizations of the references, will facilitate updating as maybe required for any future efforts associated with sulfur-modified pavement construction.

4 CONCLUSIONS

A number of typical sulfur-asphalt and sulfur-concrete paving systems were evaluated to assess their potential environmental impact and establish safety considerations relative to their formulation, construction and maintenance. Their environmental impact was investigated from the formulation stages, through weathering, and included considerations of simulated fires and chemical spills.

In the formulation phase the influence of sulfur in nine mixtures was examined against mix temperature and humidity and oxygen content of the air. The results generated in this study tend to support the data generated by others in the laboratory as well as the field; that is, that as long as the mix temperature is kept below 300°F (149°C) evolved gases and pollutants can be maintained within safe limits. These conclusions do not apply when sulfur-asphalt or sulfur concrete are processed in closed environments or stored for prolonged periods of time. Effects of humidity and oxygen were found to be negligible. The recommended maximum allowable upper temperature limit for continuous handling of sulfur modified paving materials is therefore 300°F (149°C).

It was also found that exposure to the elements had a negligible effect on these pavement materials and run-off either by wind or rain produced little or no effect on the immediate environment. It should be noted that in both the formulation and weathering studies, were maximized the results may be considered conservative.

A large number of structural materials were evaluated for possible attack by run-off from a sulfur-asphalt pavement. Of the ten materials studied, copper and steel appeared to indicate a vulnerability. The former or its alloys should never be used in equipment or structure which could bring them in contact with sulfur due to the high probability of producing the sulfates of copper. Steel reinforcing rods would be susceptible to attack by H_2SO_4 produced by moisture on contact.

The possibility of accidental events such as fire and chemical spills revealed some possible short term undesirable effects. These were in the area of obnoxious fumes or short-time-interval pollution. Both the DCPD-modified and unmodified sulfur concretes generated high levels of SO_2 during burning. Virtually all of the sulfur pavement materials were difficult to ignite and were self extinguishing.

The effect of simulated brine and gasoline spills on sulfur pavement were studied. Whereas salt based deicers would have minimal effect, organic solvents or naphtha mixtures can solubilize free sulfur.

The results of this study also produced a Field Evaluation Document (Volume II) and an Annotated Bibliography (Volume III) containing over 500 relevant sources. The Field Evaluation Document was designed for use by contractors and state agencies to establish the relative safety and for identification of potential hazards at the various locations and work elements on a sulfur-asphalt construction project. Recommended clothing and first aid procedures were included in this document.

In summary the results contained herein would tend to support the conclusion that as long as hot sulfur paving mixtures do not exceed 300°F (149°C) all sulfur originating emissions (H_2S, SO_2, SO_3 and organic sulfur materials) levels will be below their respective Maximum Allowable Concentrations. Sulfur handling practices already established in the sulfur industry as well as those common to the hot asphaltic concrete community were sufficient to assure adequate personnel safety.

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6 APPENDIX

GC-MS Analysis and Original Data on Volatilized Products from Sulfur/Asphalt Mixes

GC-MS Analysis and Original Data Sheets on Volatilized Products from Sulfur Asphalt Mixes

The products of this study were to use gas chromatograph - mass spectroscopy (GC-MS) techniques to analyze and identify compounds volatilized during formulation of sulfur-asphalt at the excessive temperature of 350°F (176°C), and compare it to asphalt alone. This was initiated in particular to identify the relatively large peak showing up by gas chromatographic (GC) analyses using the flame photometric detector in a sulfur specific mode. It should be noted that initial GC analyses (see page 53) using a flame ionization detector system revealed no hydrocarbons were in excess of 1 ppm relative to the air volume trapped. However, the sulfur constituent was definitely in excess of 1 ppm for the sulfur-asphalt material. Mix design 3 (MD-3) described in Table 11, page 39 was utilized for the comparison to the asphalt (MD-6).

Volatilized components trapped in refrigerated solvent from 2 separate formulations at 350°F were combined and concentrated by vacuum distillation for GC-MS analysis. The mass spectrometer was a Hewlett-Packard Dodecapole 5890 A model with GC inlet. It has a mass resolution of one unit mass. A 18 m glass capillary column (2 mm I.D. coated with SP 2100) was used in the GC inlet. The SP 2100 capillary column was used instead of the OV-1 material because of better resolution at one-third the time.

The resultant GC scan of MD-6 is given in appendix Figure A-1. Mass spectra of sample, both in bar diagram and in Table form, were obtained. These spectra for peaks labeled +527, +583, +784, +859, +872 and +914 in Figure A-1 are given in Figures A-2, A-3, A-4, A-5 and A-6, respectively. These spectra were first compared with the 19,000 known mass spectra listed in "Registry of Mass Spectra Data" by S. Abrahamson; E. Stenhagen; F. W. McLafferty; Wiley, N. Y. 1974. Cornell University's computer program for mass spectra identification - PBM was also used to interpret some of MS obtained. The PBM has a data bank of 41,429 known mass spectra. Through telecommunication every known spectra in the data bank was retrieved and compred to the mass spectrum obtained. No match was ever found due principally to the low concentrations in combination with background matrix effects. However, possible structures were had computed from crack patterns for peaks labeled +527, +784, +872 and +914 (Figure A-1). The results of this effort are summarized in Table A-1. Of note is the fact that sulfur does not dominate any of the mass spectra, but did show up as moiety of peaks +784 and +914. The asphalt material was shown to contain approximately 0.5% sulfur.

The resultant GC scan of MD-3 is given in appendix Figure A-7. Adjustments were made to increase sensitivity levels of the flame ionization detector. An attempt was made to obtain the mass spectrum of a peak with a retention time of 15.5 minutes. The spectrum shown in Figure A-8 shows sulfur to dominate as a background. The initial mass spectrum for peak labeled +585 was initially dominated by sulfur Figure A-9. A second run negating the sulfur background is given in Figures A-10. The spectrum shows a similar framenting pattern as that noted for peak +527 obtained for the MD-6 sample. Mass spectrum of peak +638 is given in Figure A-11. Results of spectra are given in Table A-2.

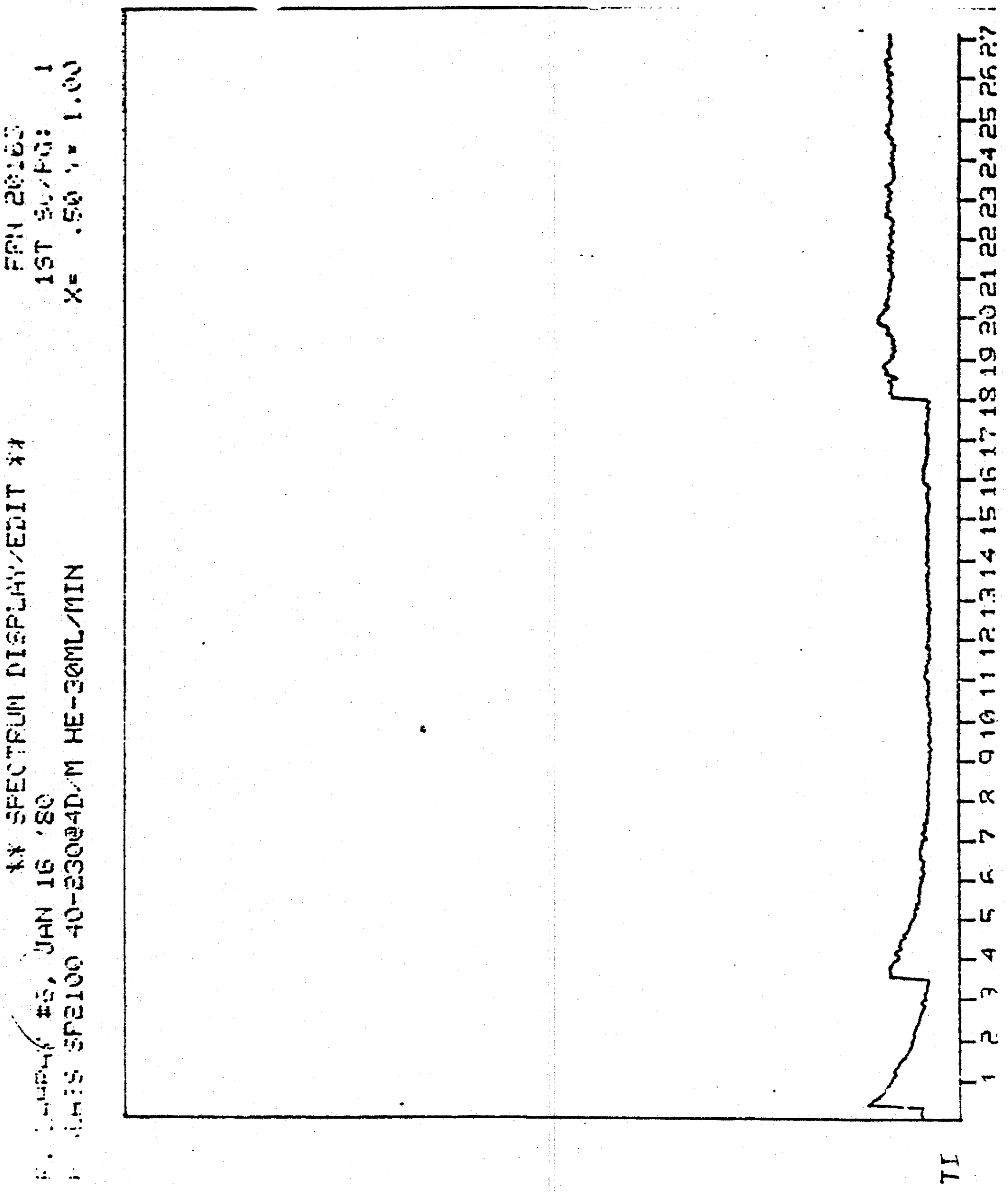
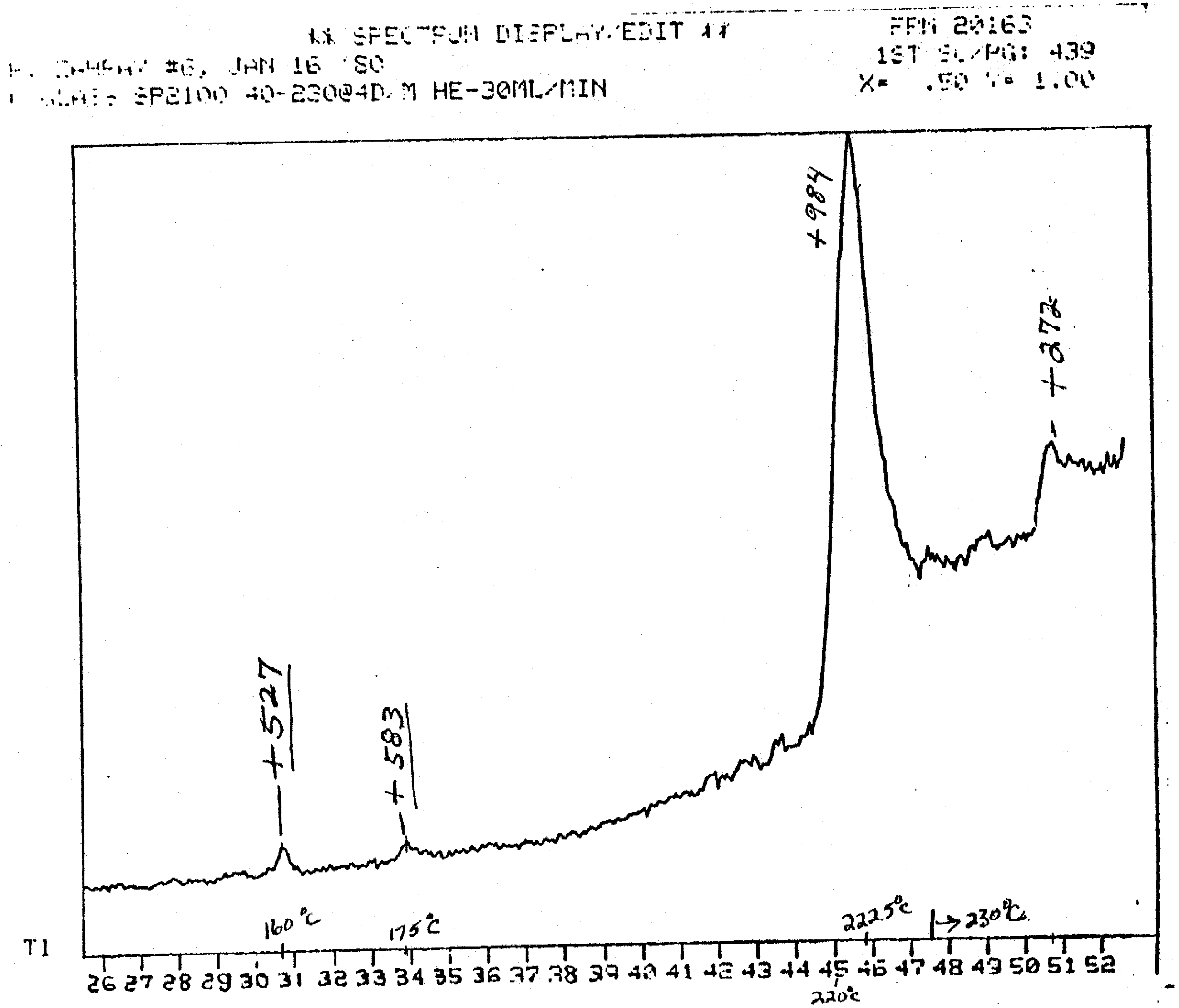


Figure A-1. Gas Chromatographic Scan of MD-6.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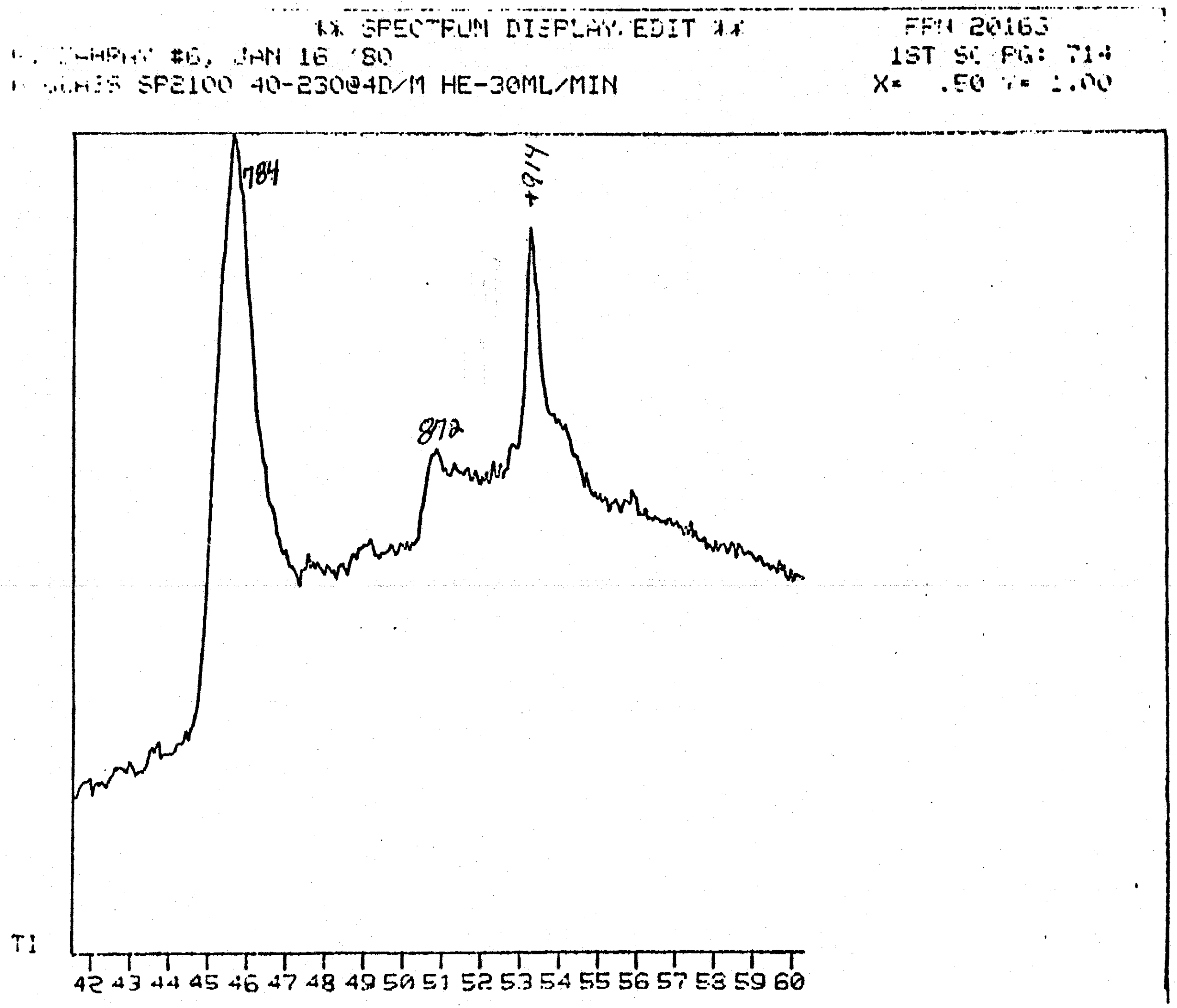
#6, JAN 16 '80
SP2100 40-230@4D/M HE-30ML/MIN
FRN 20163
1ST SC/PG: 439
X= .50 Y= 1.00
+527
+583
+984
+272
160 °C
175 °C
222.5 °C
→ 230 °C
220 °C
TI
26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52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FRN 20163
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1ST SC PG: 714
[illegible] SP2100 40-230@4D/M HE-30ML/MIN
X= .50 Y= 1.00
784
872
+914
TI
42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

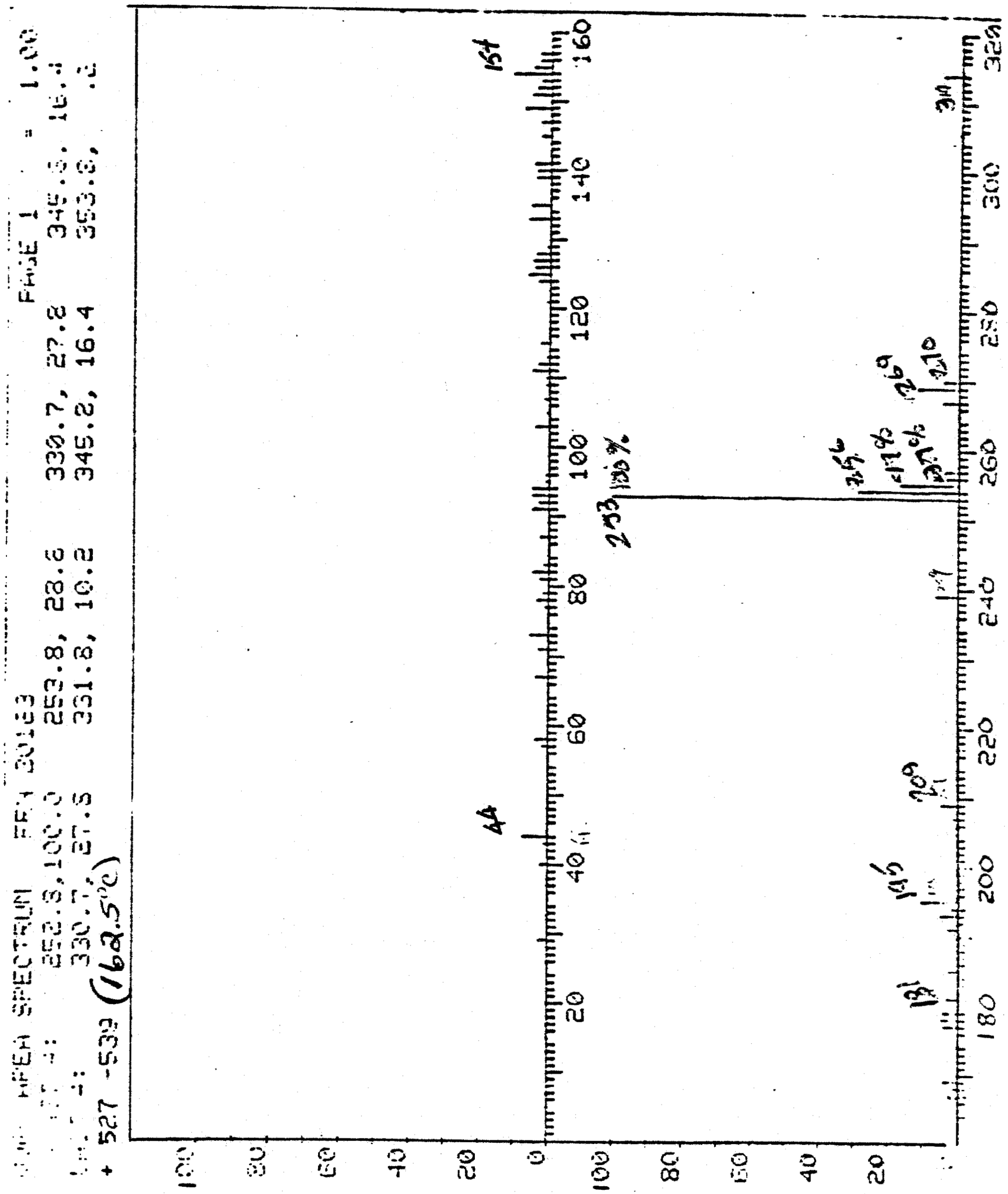


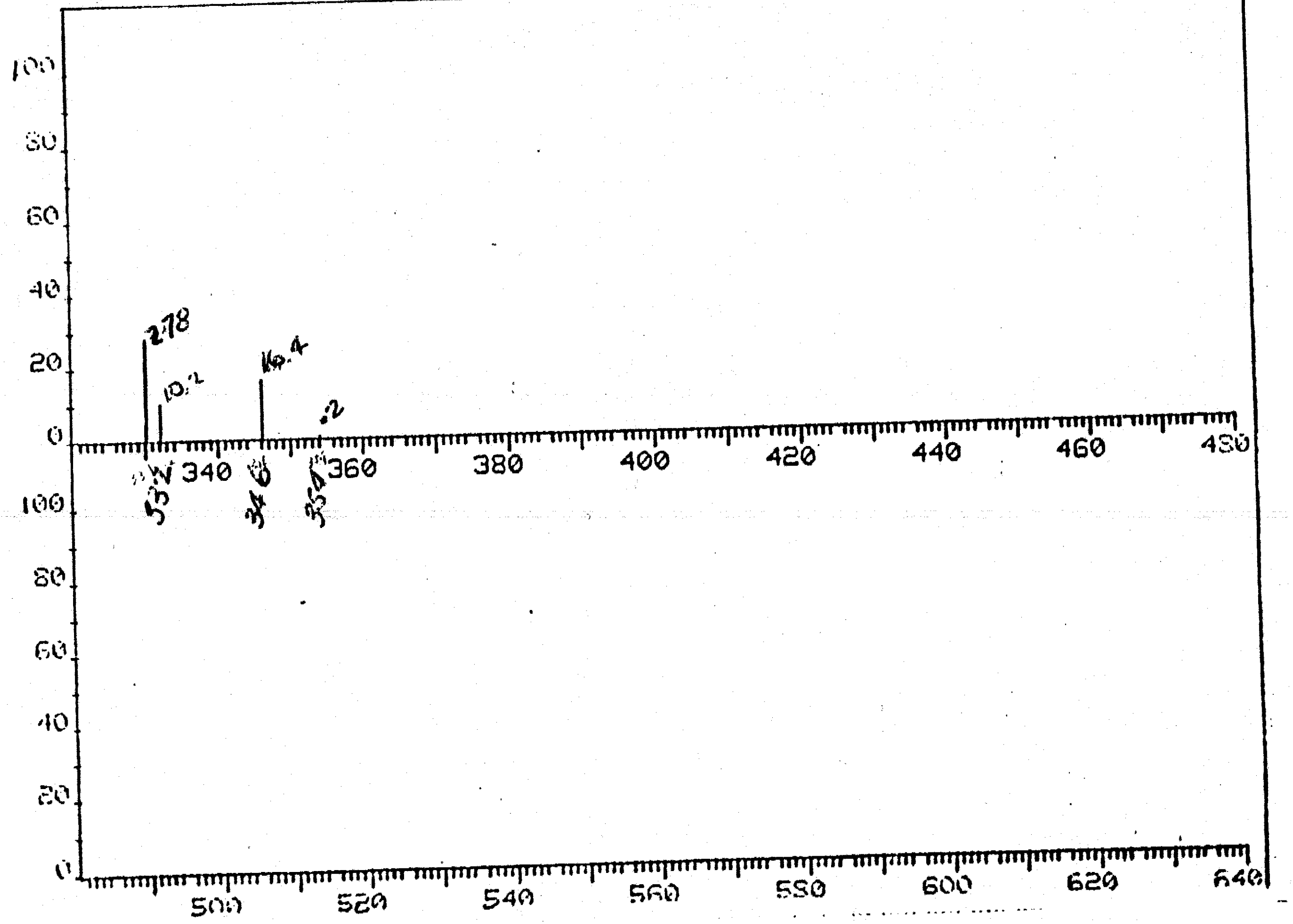
Figure A-2. Mass Spectrum of Peak +527.

WORK AREA SPECTRUM FRN 20163 PAGE 2 Y = 1.00

TARGET #: 252.8,100.0 253.8, 28.6 330.7, 27.8 345.3, 16.4

LAST #: 330.7, 27.8 331.8, 10.2 345.8, 16.4 353.8, .2

+ 527 -539 (162.5°C



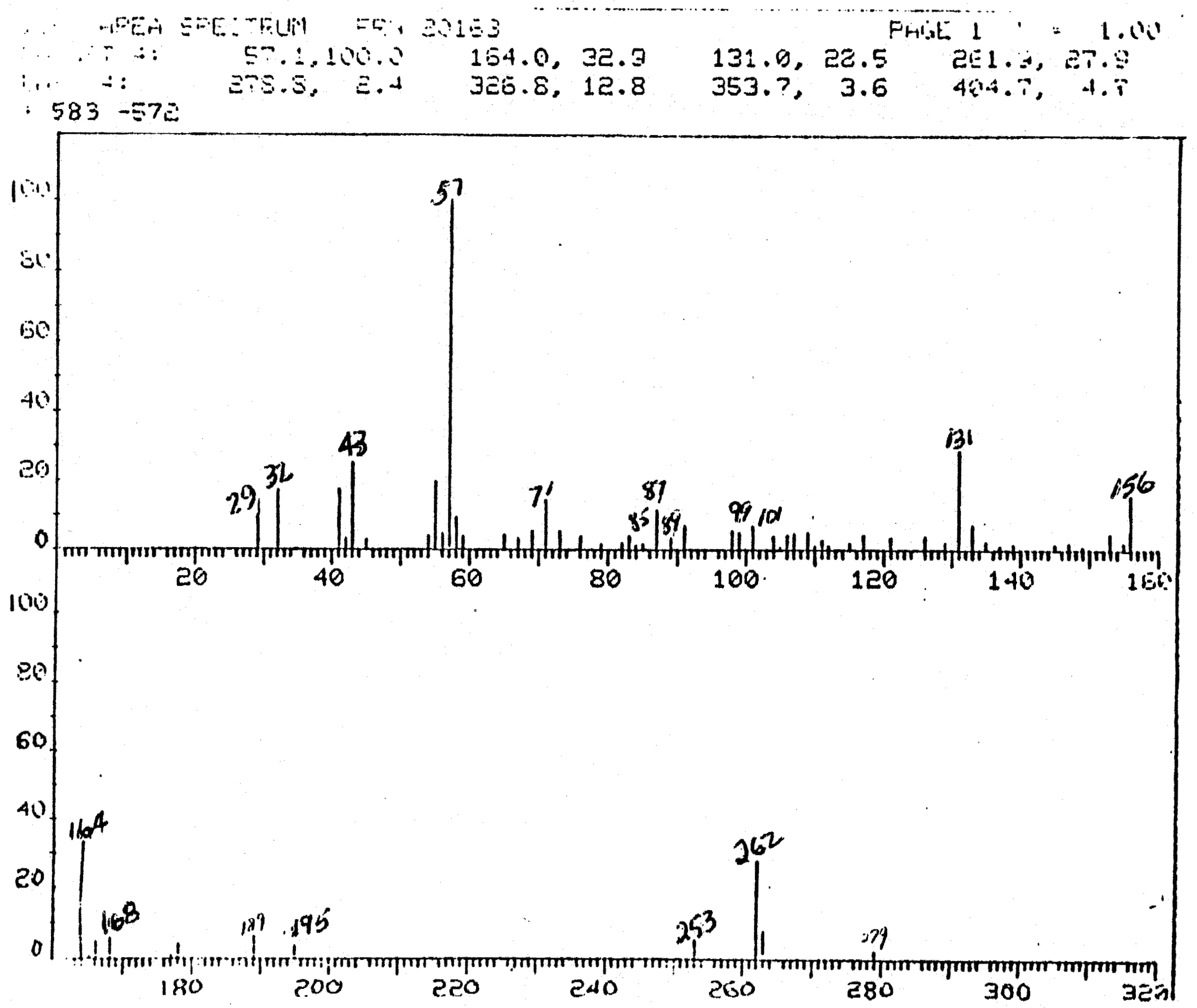
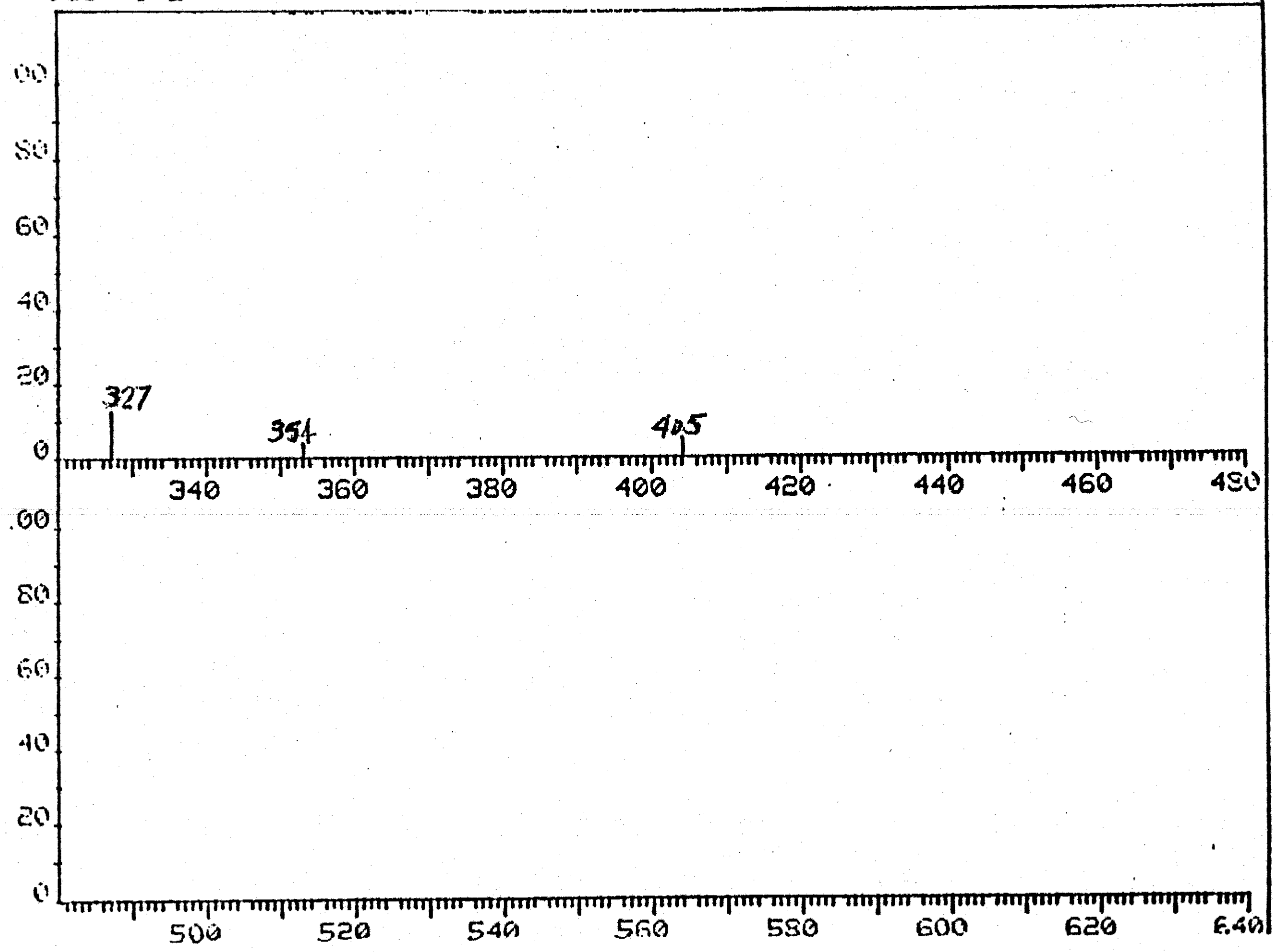


Figure A-3. Mass Spectrum of Peak +583.

```
WORK AREA SPECTRUM   FRN 20163                          PAGE 2  Y =  1.00
LARGEST 4:     57.1,100.0   164.0, 32.9   131.0, 28.5   261.9, 27.9
LAST 4:       278.8,  2.4   326.8, 12.8   353.7,  3.6   404.7,  4.7
+ 503 -572
```



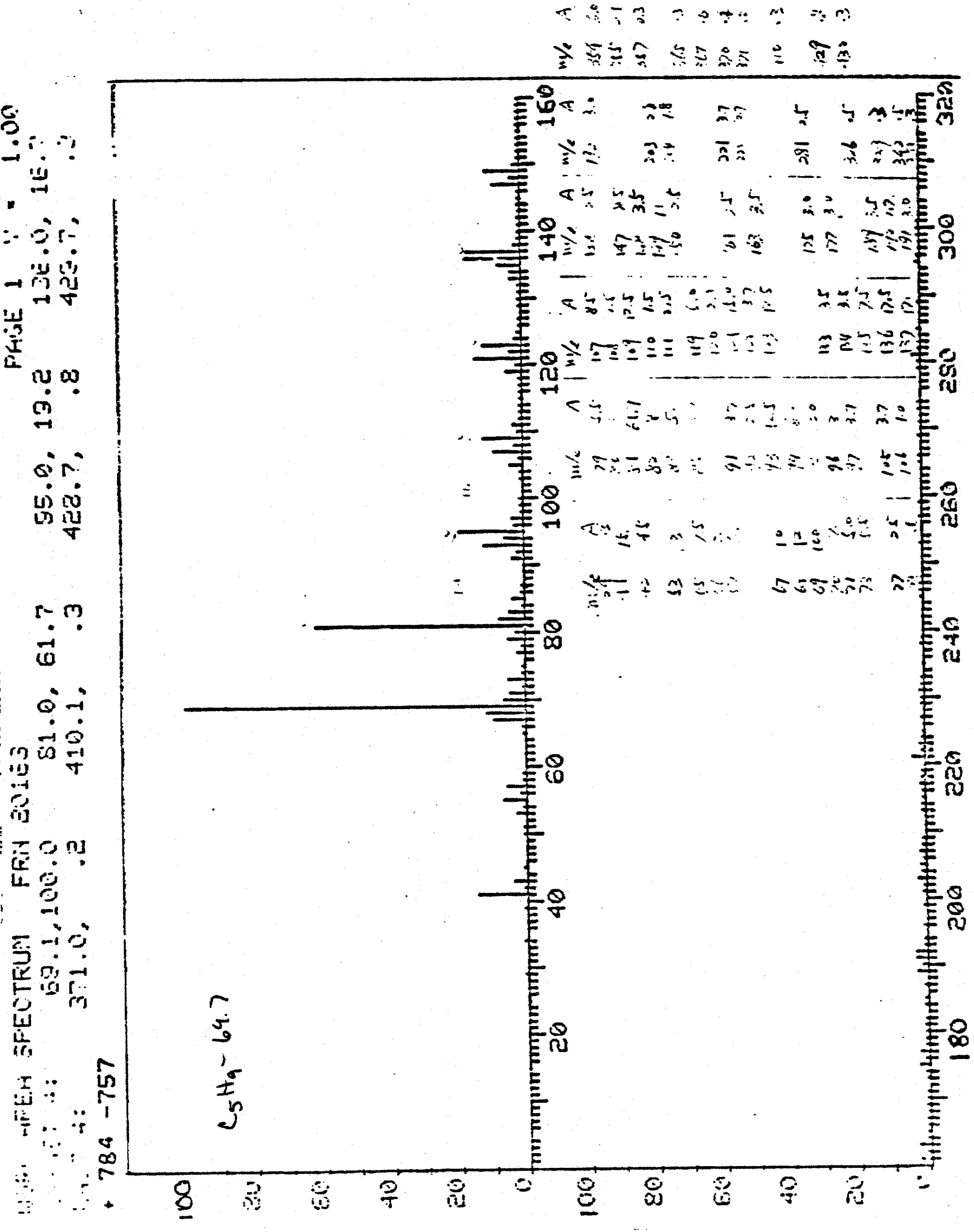
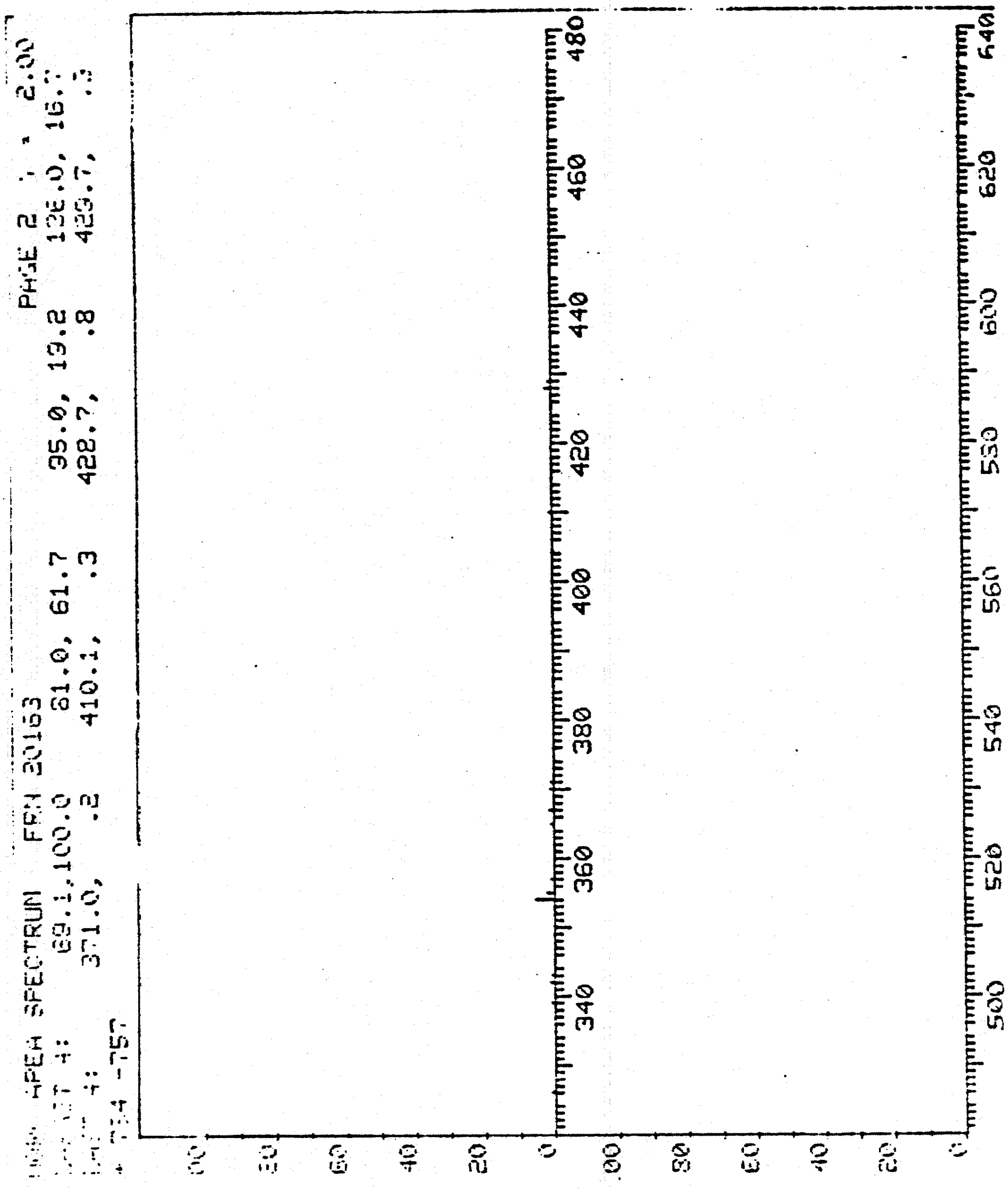


Figure A-4. Mass Spectrum of Peak +784.


AREA SPECTRUM FRN 30163 PAGE 2 2.00
69.1,100.0 81.0, 61.7 95.0, 19.2 136.0, 16.7
371.0, .2 410.1, .3 428.7, .8 429.7, .3
-757
0
20
40
60
80
100
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640

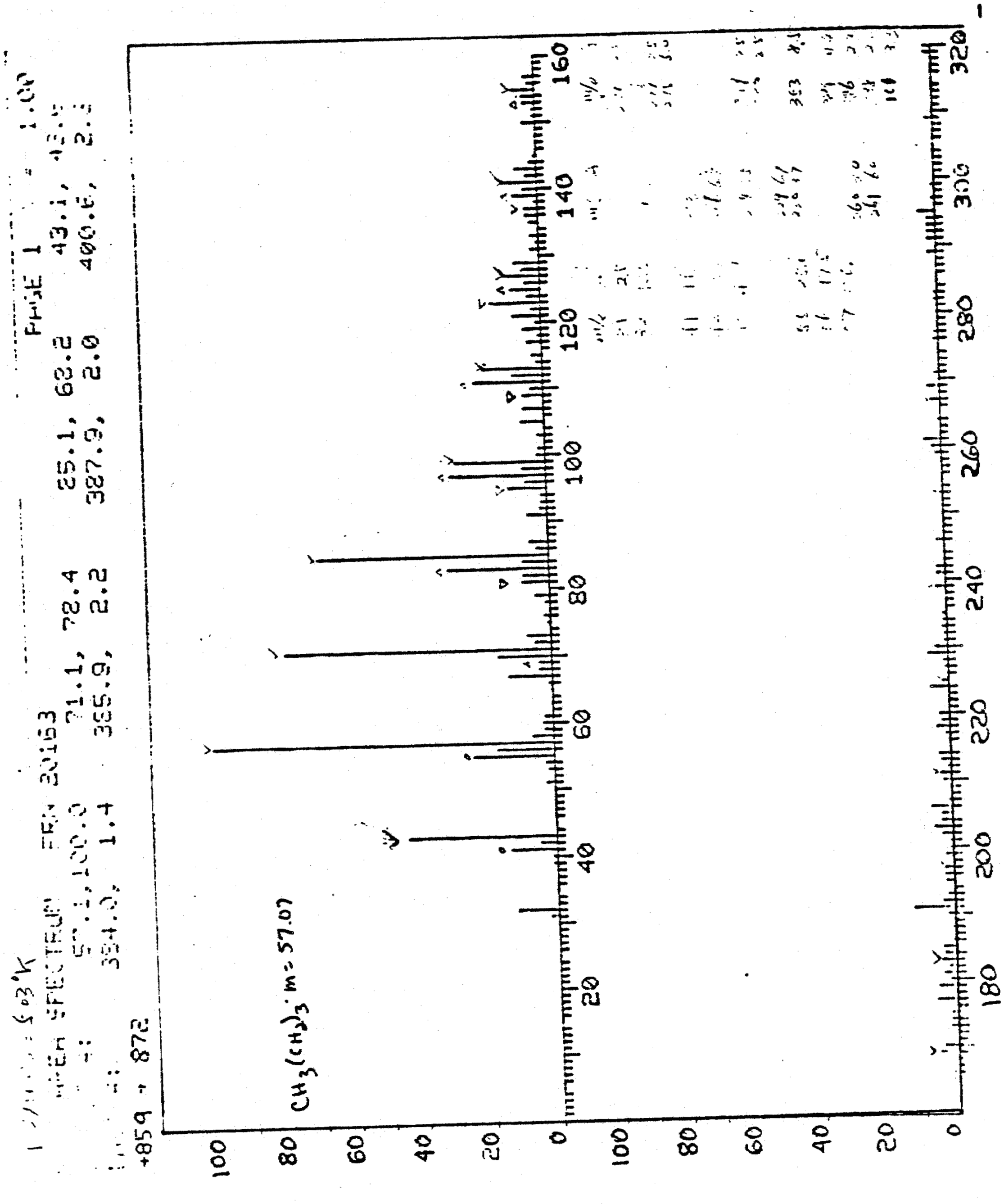
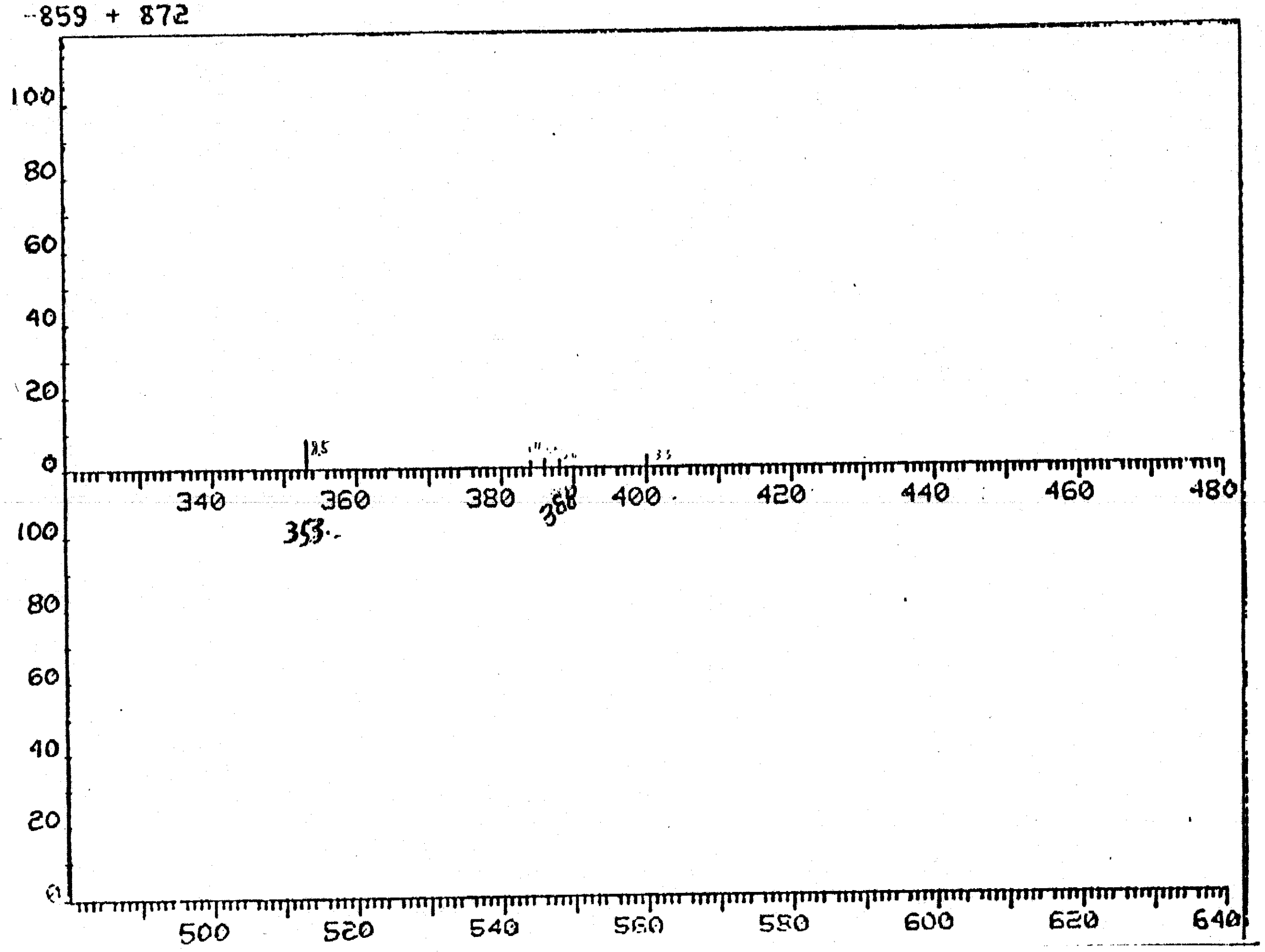


Figure A-5. Mass Spectrum of Peak +859.

```
NORM AREA SPECTRUM   FRN 20163                                 PAGE 2  % ·  1.00
TARGET #:      57.1,100.0     71.1, 78.4     85.1, 62.2     43.1, 43.6
LAST #:        384.0,  1.4    385.9,  2.2    387.9,  2.0    400.6,  2.8
-859 + 872
```



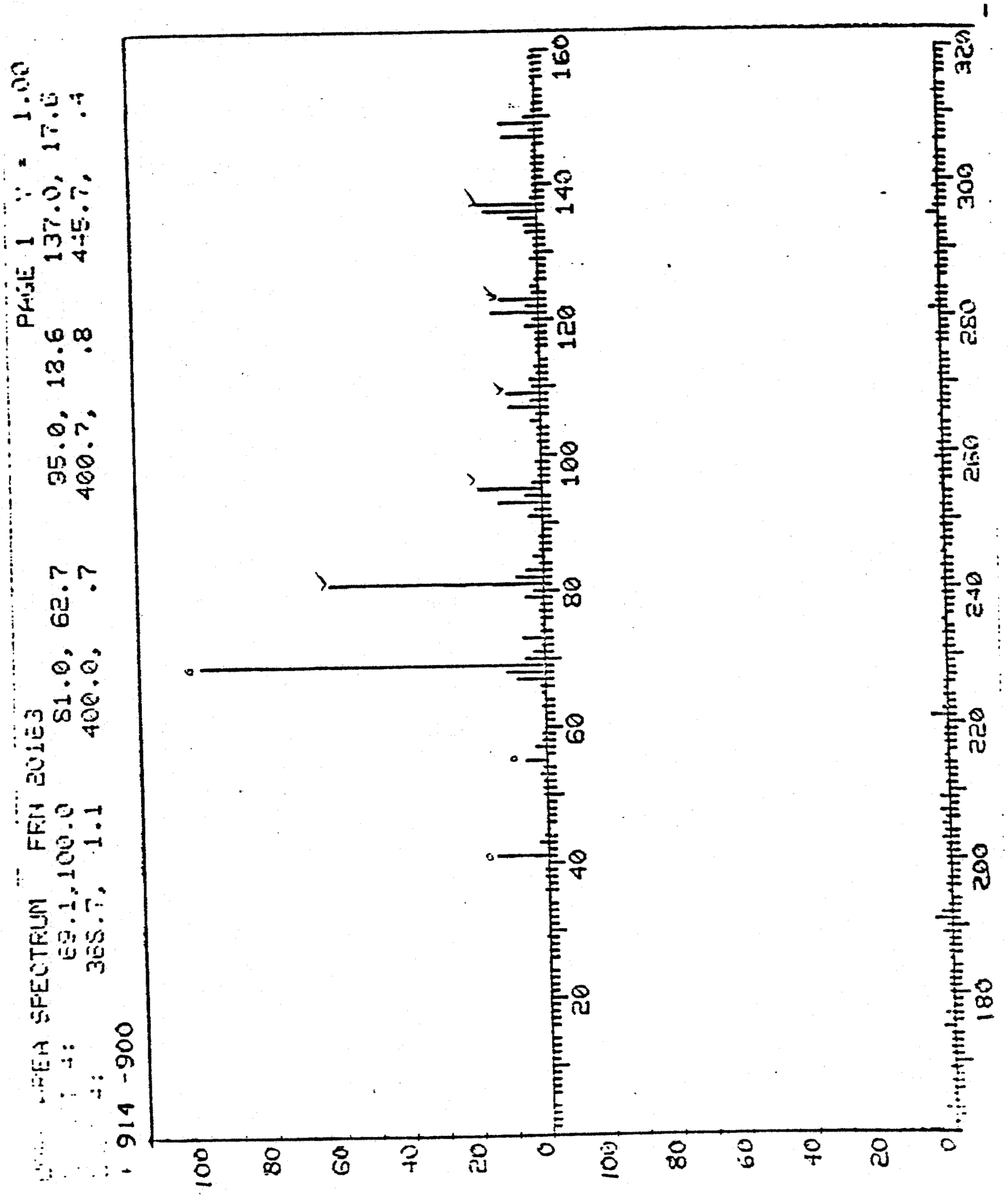


Figure A-6. Mass Spectra of Peak +914.

```
NORM AREA SPECTRUM   FRN 20183                                  PAGE 2  % =  2.00
[illegible] 4:      69.1,100.0      81.0, 62.7      95.0, 18.6     137.0, 17.6
[illegible] 4:     365.7,  1.1     400.0,   .7     400.7,   .8     445.7,    .4
+ 914 -900
```

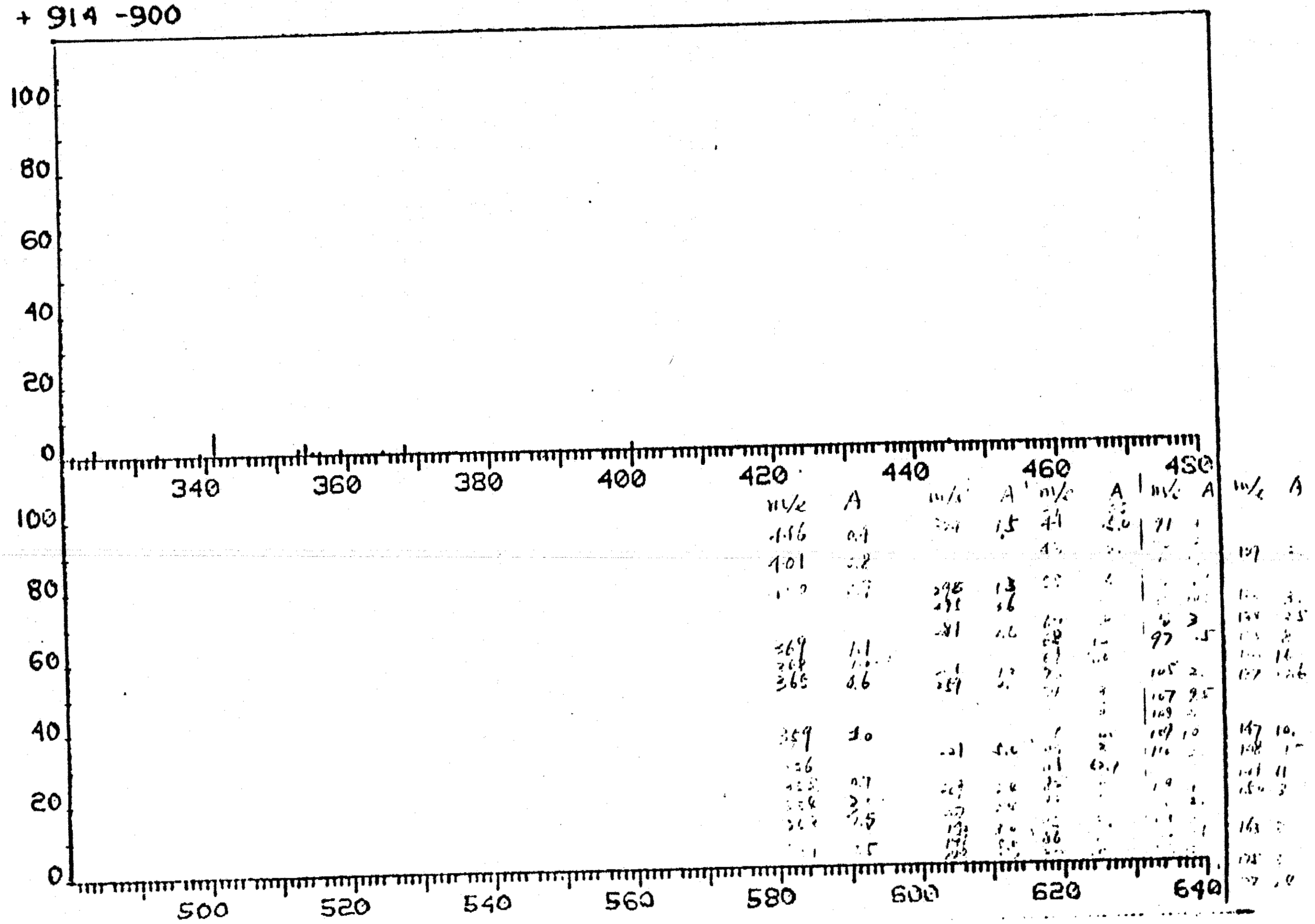
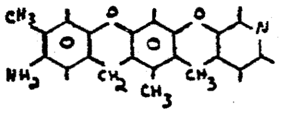
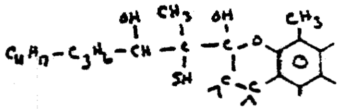
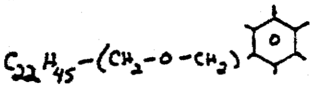
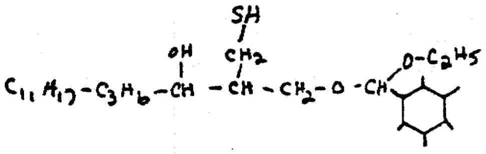


Table A-1. Summary of Mass Spectra of MD-6.

Peak no.	Retention Time (min)	Mass	Possible Structure
+527	30.7	346	
+784	45.7	444	
+872	50.9	430	
+914	53.4	446	

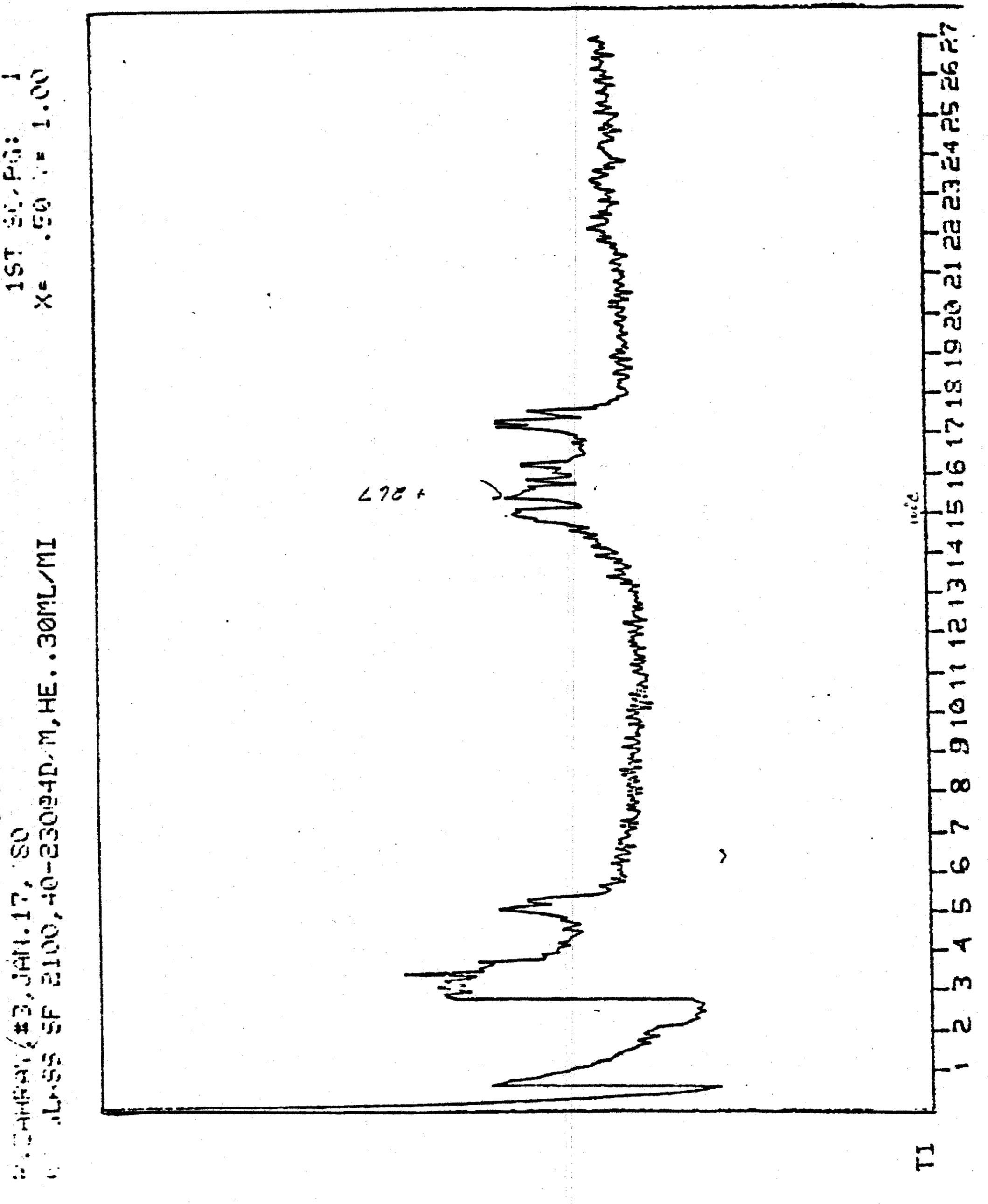
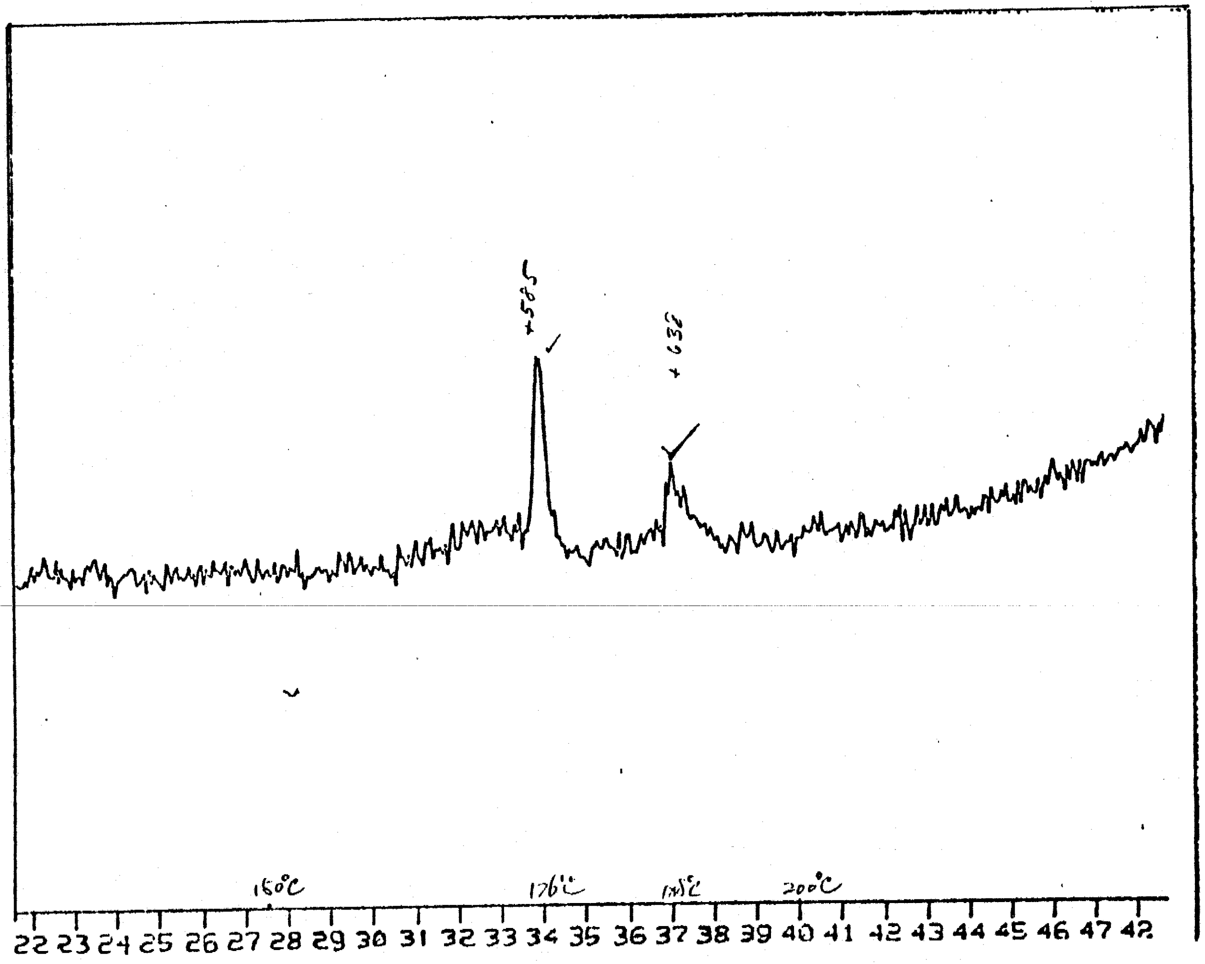
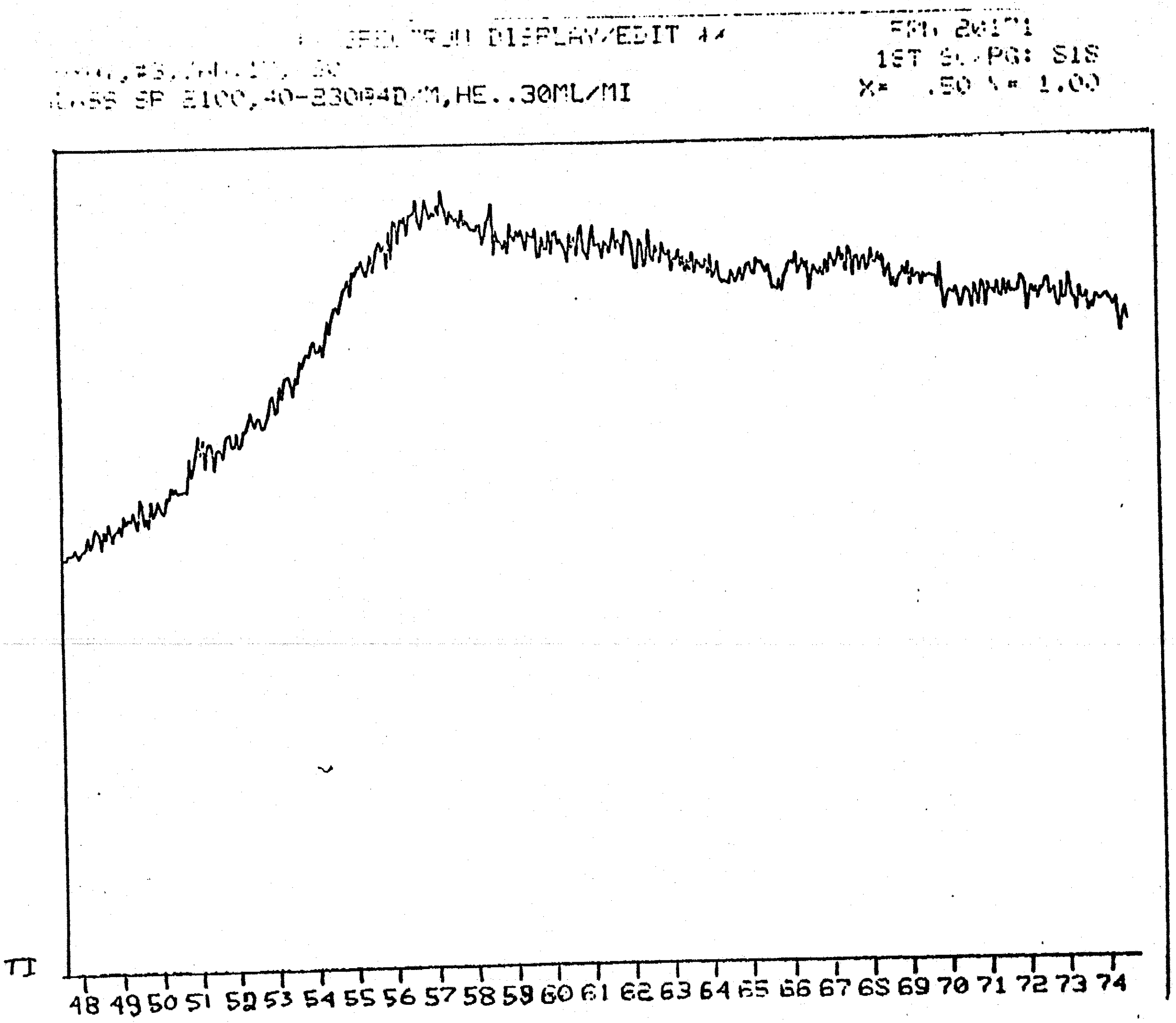


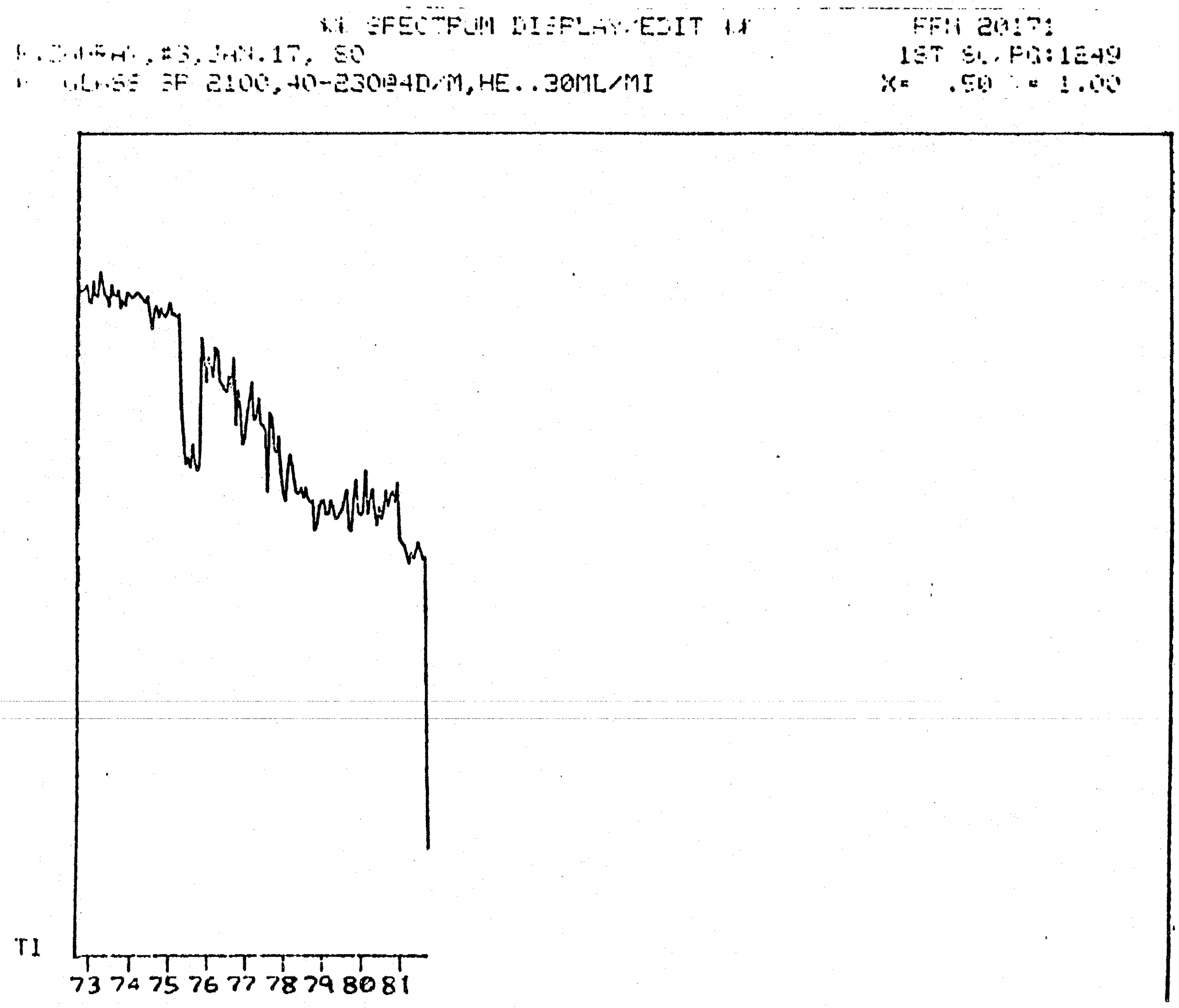
Figure A-7. Gas Chromatographic Scan of MD-3.

** SPECTRUM DISPLAY/EDIT **
[illegible],#3,JAN.17, 80
[illegible] GLASS SP 2100,40-230@4D/M,HE..30ML/MI

FRN 20171
1ST SC RG: 372
X= .50 - 1.00




DISPLAY/EDIT
1ST PG: S18
X= .50 = 1.00
SP E100,40-230@4D/M,HE..30ML/MI
TI
48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74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FFN 20171
#3,JAN.17, 80
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SF 2100,40-230@4D/M,HE..30ML/MI
X= .50 = 1.00
T1
73
74
75
76
77
78
79
80
81

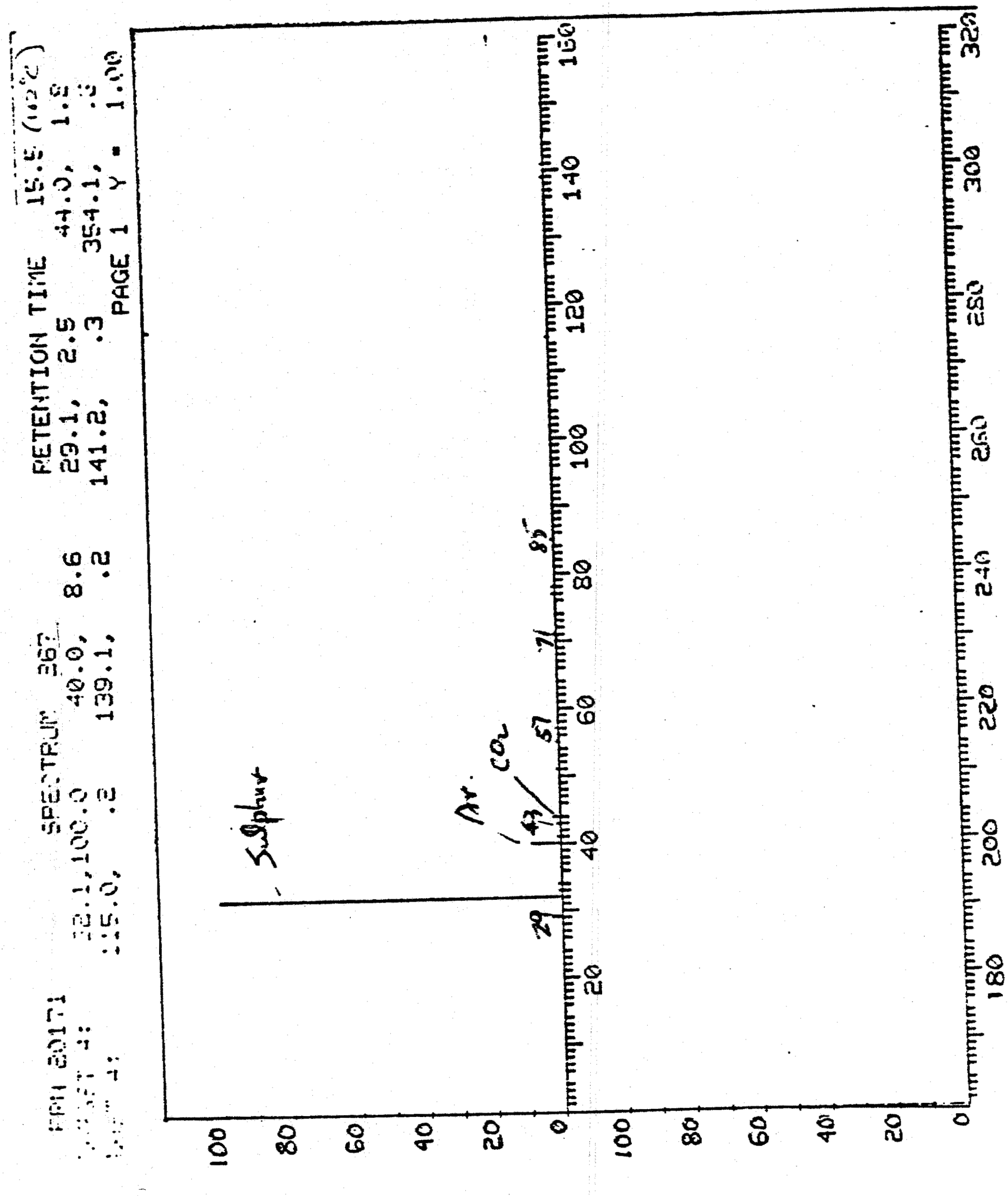


Figure A-8. Mass Spectrum of Peak +267.

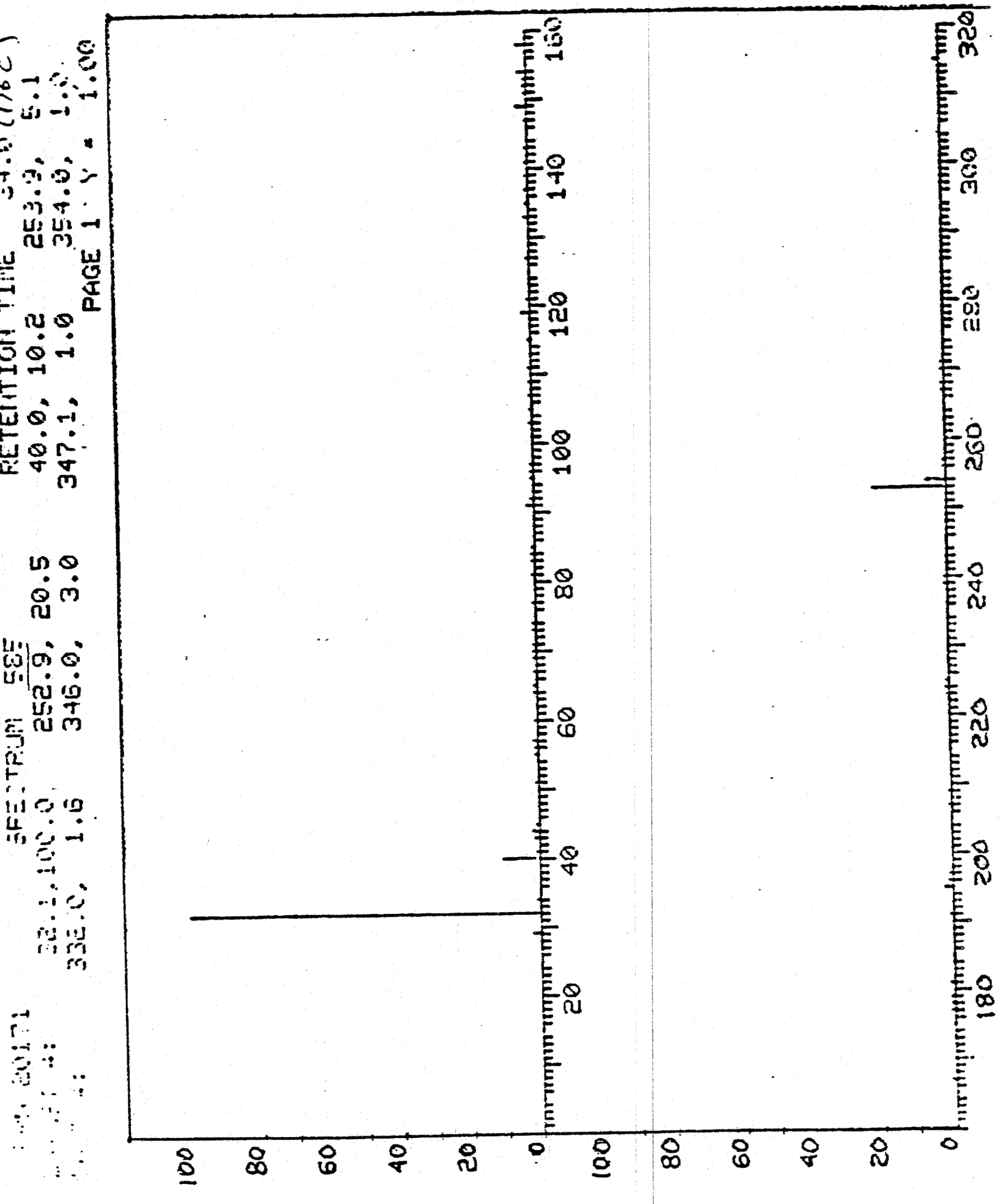
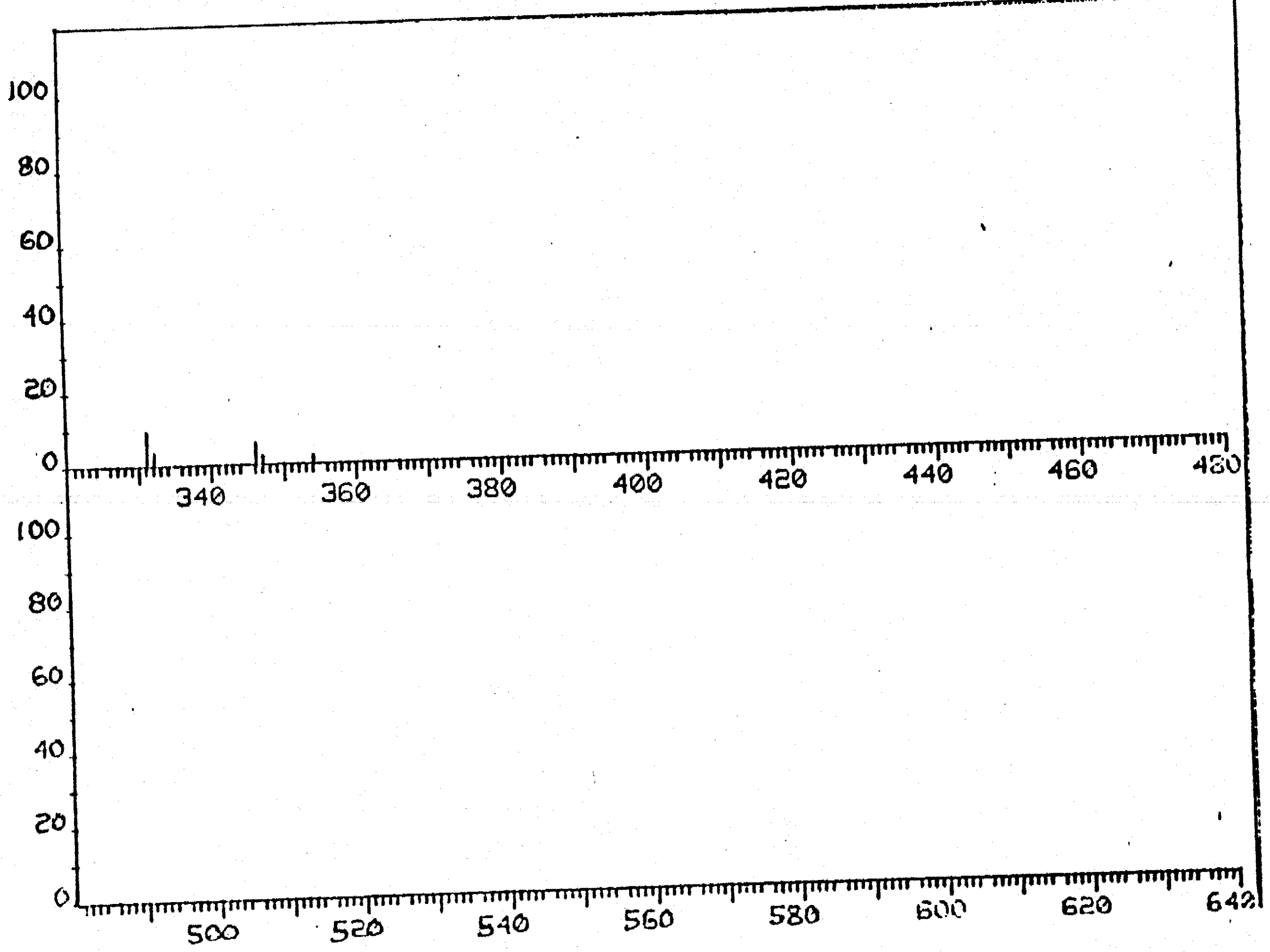


Figure A-9. Mass Spectrum of Peak +585.

```
FRN 20171              SPECTRUM  585              RETENTION TIME   34.0 (176°c)
LARGEST 4:       32.1,100.0     252.9, 20.5     40.0, 10.2     253.9,  5.1
[illegible] 4:   332.0,  1.6     346.0,  3.0    347.1,  1.0     354.0,  1.0
                                                             PAGE 2  Y =  2.00
```



RT 31/10

```
[illegible] AREA SPECTRUM   FRN 30171                              PAGE 1       1.00
[illegible]:     352.9,100.0     253.9, 24.5     331.0, 22.1     143.0, 17.5
[illegible]:     331.0, 22.1     332.0,  7.4     346.0, 15.3     347.1,  6.2
+ 585 -570
```

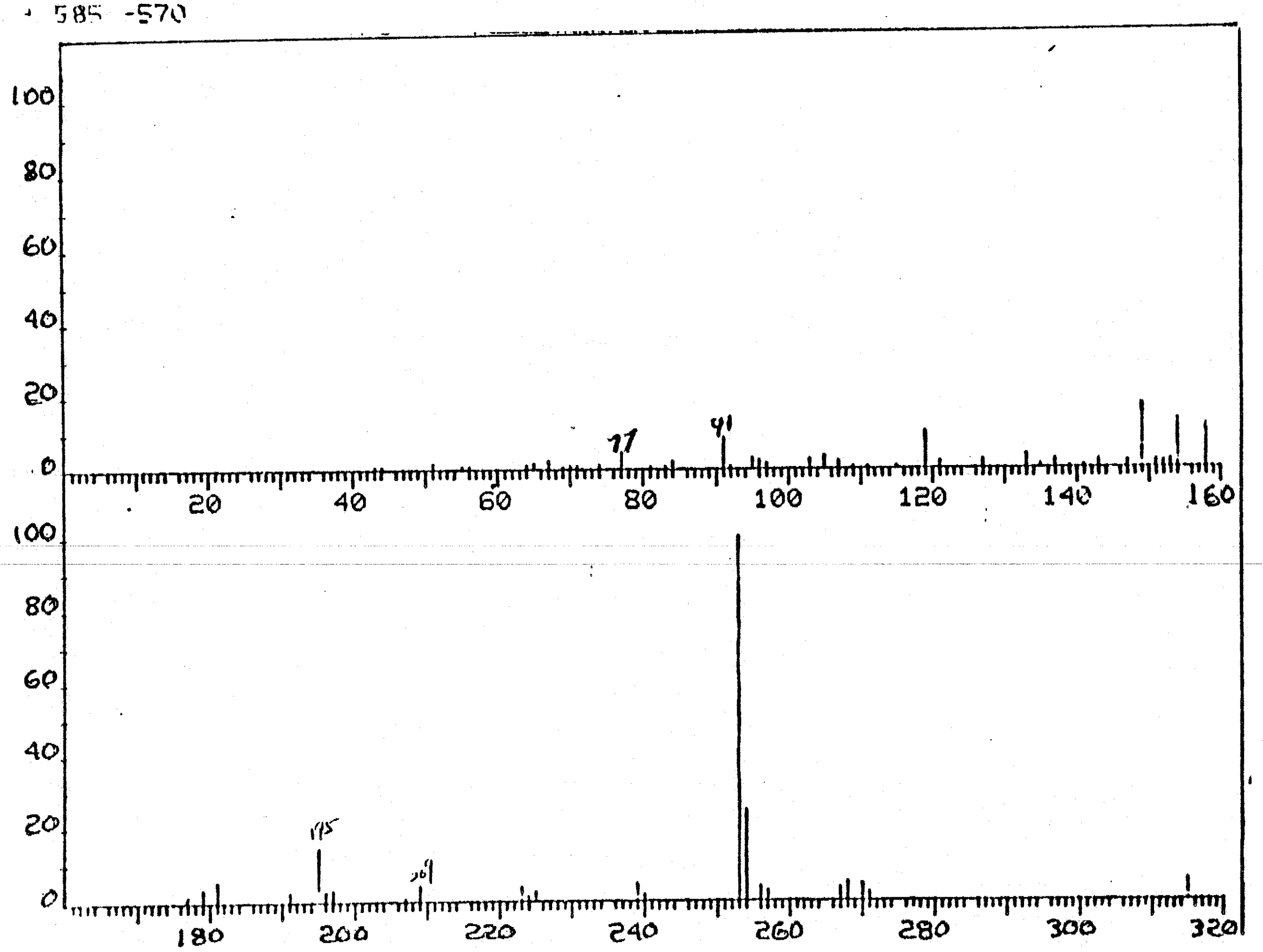
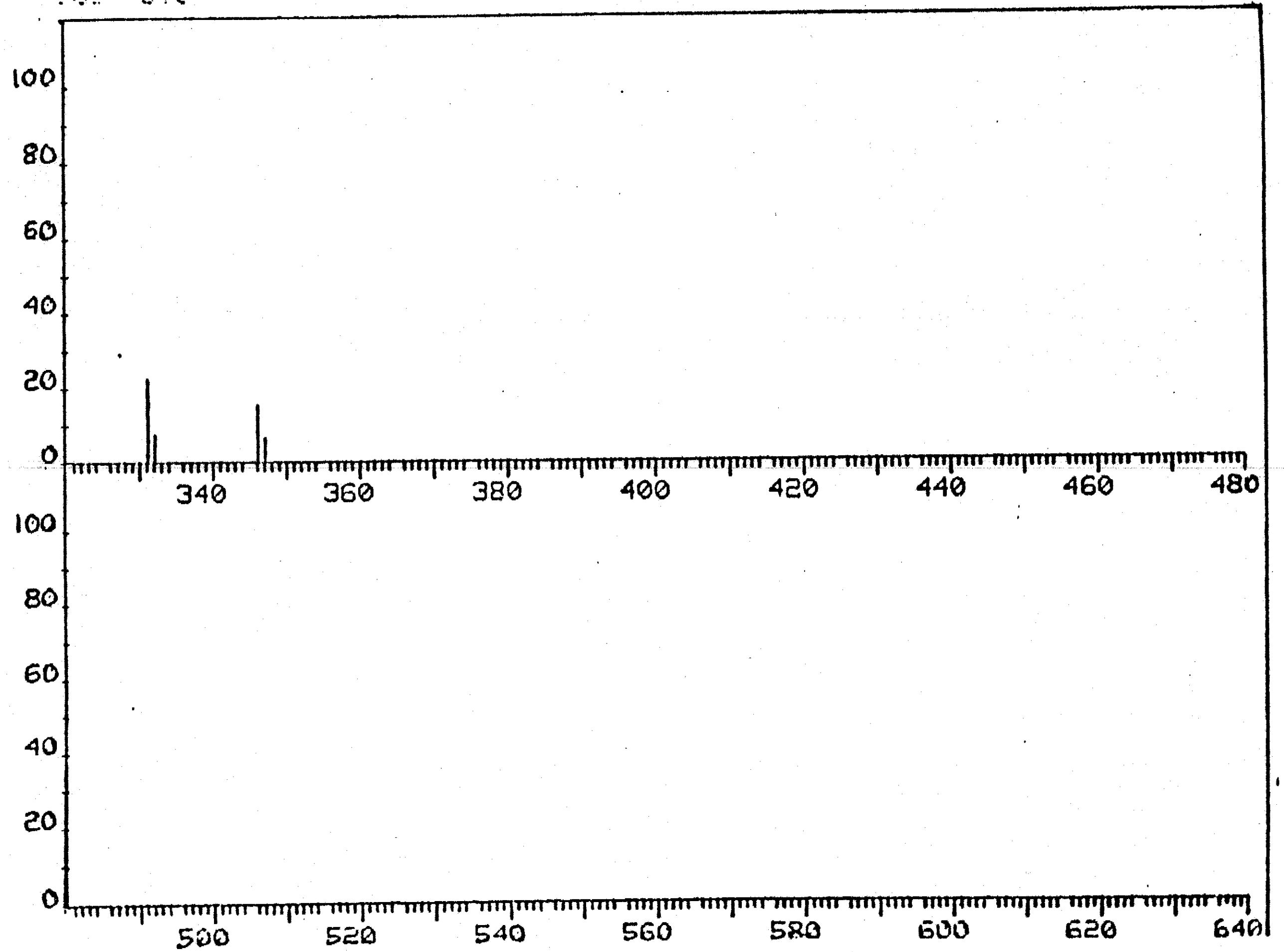


Figure A-10. Mass Spectrum of Peak +585, second run.

RT 34.0

```
WORK AREA SPECTRUM   FRN 20171                                      PAGE 2  % =  1.00
LARGEST 4:     252.9,100.0     253.9, 24.5     331.0, 22.1     149.0, 17.5
LAST 4:        331.0, 22.1     332.0,  7.4     346.0, 15.3     347.1,  6.2
+ 535 -570
```



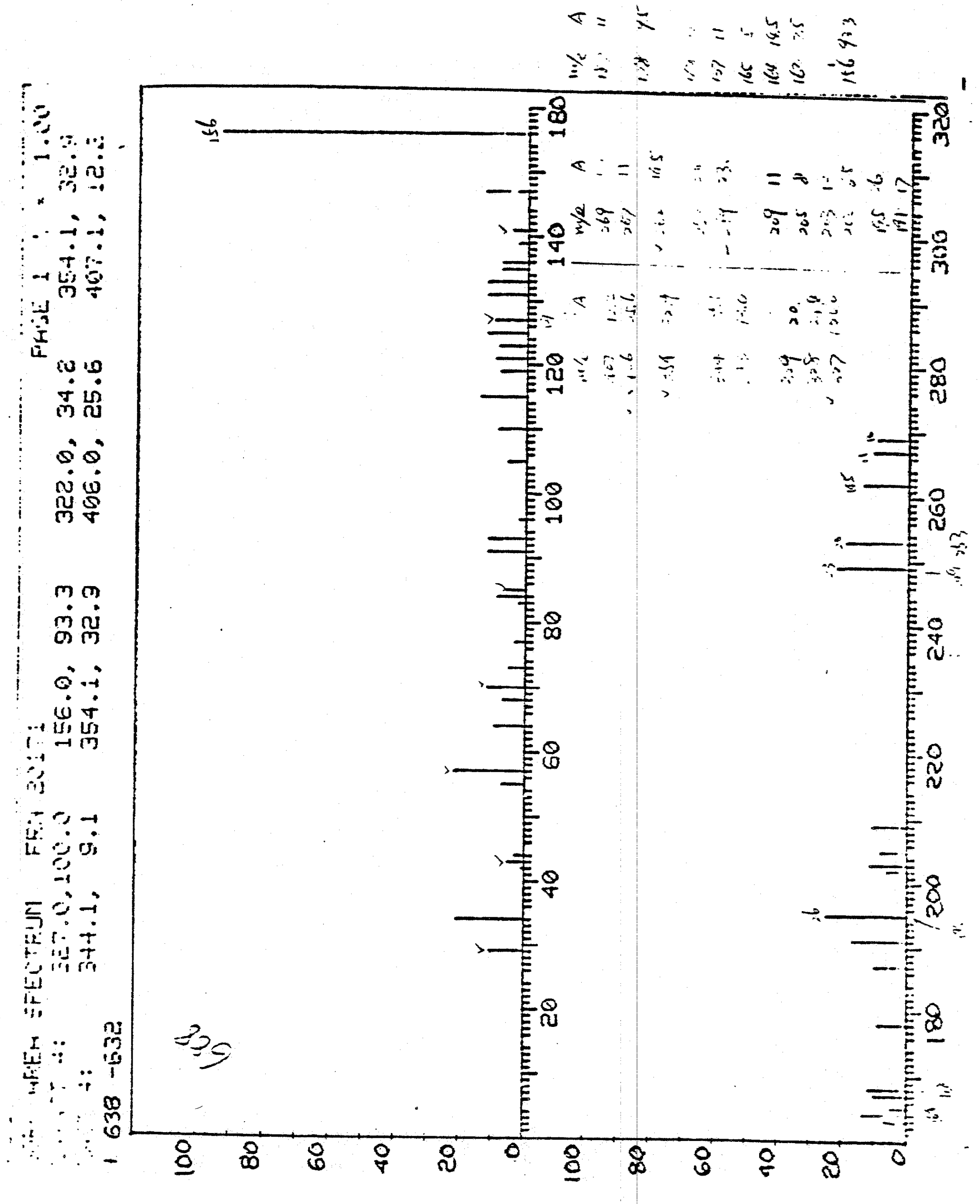


Figure A-11. Mass Spectrum of Peak +638.

RT 370

```
NORM. AREA SPECTRUM   FRN 20171                                   PAGE 2  Y =  1.00
TARGET 4:      327.0,100.0     156.0, 93.3     328.0, 34.8     354.1, 32.9
[illegible] 4:      344.1,  9.1     354.1, 32.9     406.0, 25.6     407.1, 12.2
+ 638 -632
```

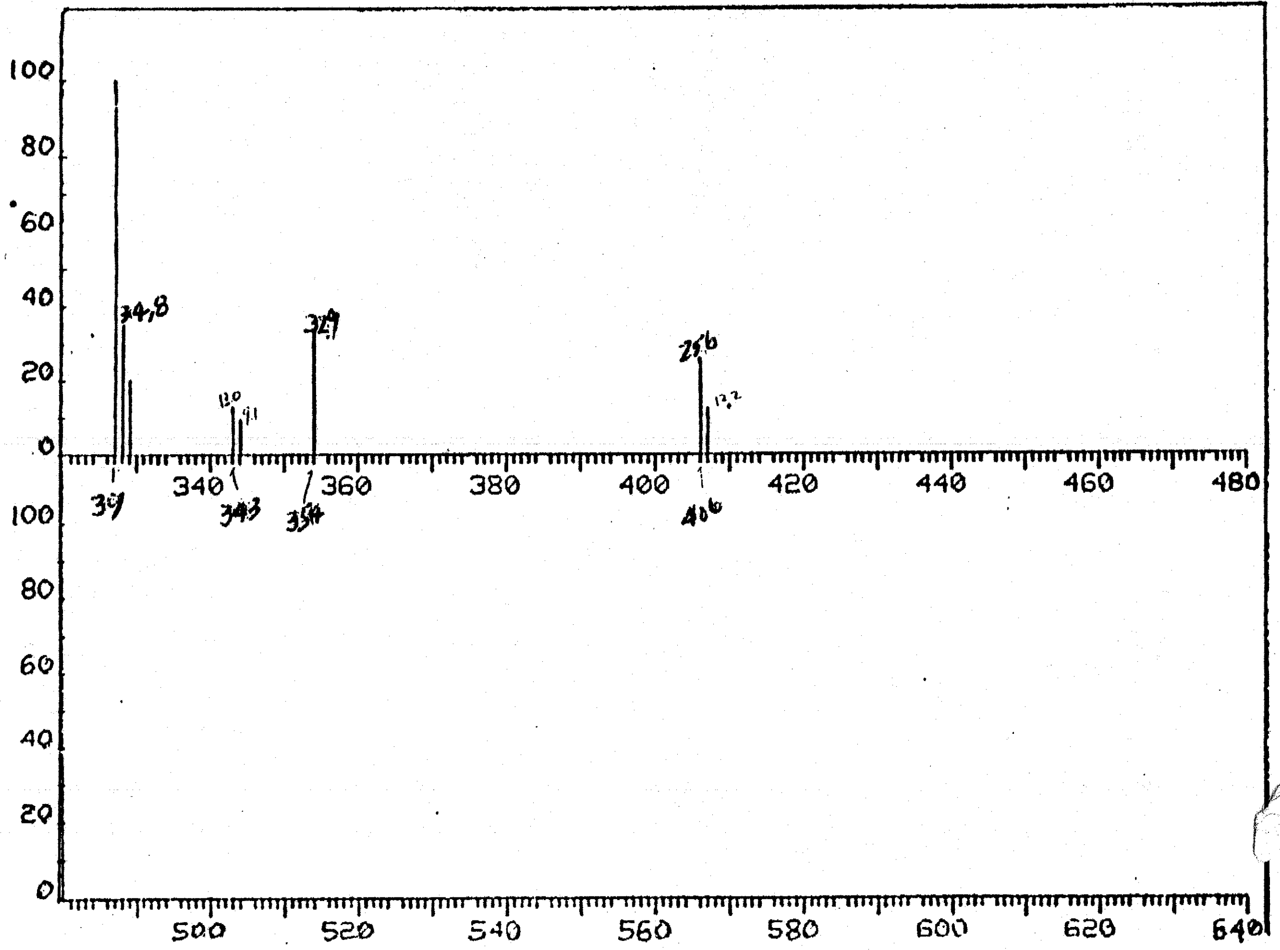
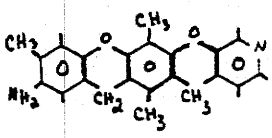


Table A-2. Summary of Mass Spectra for MD-3.

Peak no.	Retention Time (min)	Mass	Possible Structure
+267	15.5	32	Sulfur dominated spectra
+585	34	346	
+638	37	434