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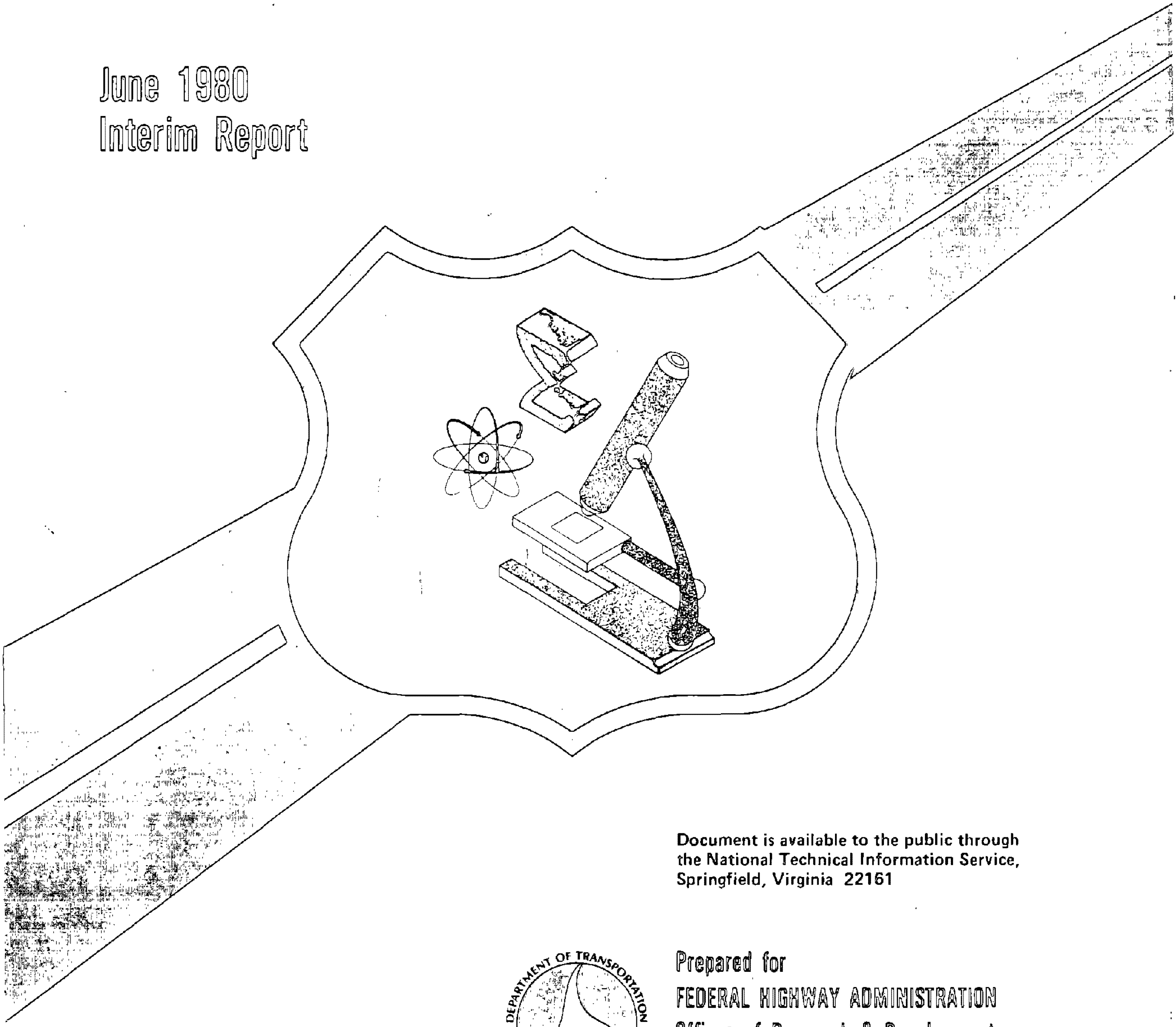
MATERIALS AND TECHNIQUES FOR IMPROVING THE ENGINEERING PROPERTIES OF SULFUR

June 1980
Interim Report



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DEPARTMENT OF TRANSPORTATION
UNITED STATES OF AMERICA

Prepared for
FEDERAL HIGHWAY ADMINISTRATION
Offices of Research & Development
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Washington, D.C. 20590

FOREWORD

This report presents the findings of an FHWA administrative contract research study conducted by Southwest Research Institute (SWRI) in which a family of modified sulfur binders (Sulphlex) were developed. The findings will be of interest to researchers and operations personnel concerned with the task of identifying alternatives to asphalt or portland cement.

The data presented herein on the physical properties of the various Sulphlex formulations and of mixtures of these binders with aggregates are based on a very limited volume of tests. Many things are still unknown about this new family of materials such as reproducibility of the material in batch sizes larger than those that can be formulated in a chemcial laboratory. Also, appyling tests that were developed for evaluation of asphalt or asphaltic mixtures to Sulphlex may not be valid. Accordingly, further testing may not duplicate the results given herein. However based on the results of the SWRI laboratory research and the short test road constructed at SWRI in December of 1978 it is warranted to continue our efforts to exploit the research results with cautious optimism.

This report is being distributed in sufficient numbers to provide a minimum of one copy to each regional office and division office and two copies to each State highway agency. Additional copies of the report for the public are available from the National Technical Information Service (NTIS), Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

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Director, Office of Research

NOTICE

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16. Abstract

Asphalt and Portland cement are the principal binders used in the preparation of pavements. The costs of these materials are directly related to energy and are expected to increase. The availability of asphalt in the future in the event of an oil embargo or other crisis is questionable. Native as well as by-product sources of sulfur in the United States are large and are expected to increase in the future. Sulfur in its elemental form is not ideally suited for use as a pavement binder because of its brittle and friable nature. This program was undertaken to determine if elemental sulfur could be inexpensively modified so it could be used as a pavement binder. As a result of this work, a new pavement binder system, based on elemental sulfur, has been developed that can serve as a replacement for asphalt and Portland cement. This material can be emulsified with water and used like asphalt emulsions.

17. Key Words
Sulfur, Polymerization, Modified sulfur, roadway binders, asphalt replacement, SULPHLEX

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INTRODUCTION

This program was undertaken to chemically modify elemental sulfur to improve its engineering properties for the purpose of providing:

1. A binder to serve as a replacement for asphalt in flexible paving mixtures.
2. A binder to serve as a replacement for Portland cement in rigid paving mixtures.

Promising results in meeting both of these objectives have been achieved. For identification purposes, the developed binder material has been named "SULPHLEX". In addition to its potential as a replacement for asphalt and Portland cement, more limited experimental work indicates it has potential as an asphalt extender in water emulsions and as an asphalt rejuvenator, thus providing several alternate routes for its use in the paving industry. Figure 1 is a chart of how SULPHLEX is produced and how it is envisioned as being used.

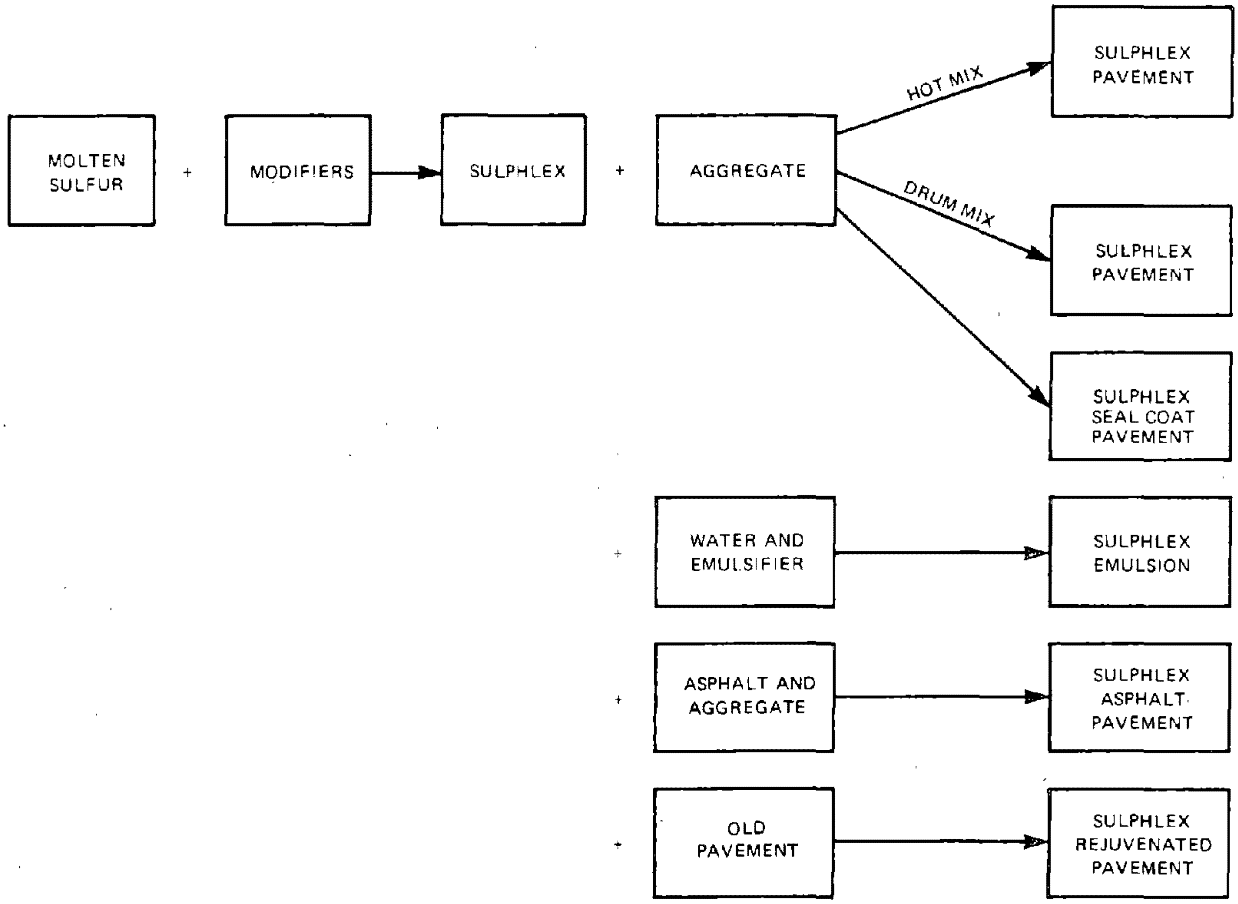

Figure 1. SULPHLEX production and potential uses.

An extension was made to the contract to lay a 620 ft (189 m) experimental roadway using three different SULPHLEX formulations. This roadway was successfully installed in December 1978. The work describing that installation is included in Appendix A.

This research should not be confused with the considerable amount of previous work that has been done in the physical-mechanical addition of elemental sulfur to asphalt to produce sulfur extended asphalt (SEA) pavements. Principals in that work have been Gulf Oil Company, Shell®Oil Company, Elf Aquitaine, the U.S. Bureau of Mines and others. Their work has been extensively documented and is readily available in the literature.

LITERATURE REVIEW (Task A)

A "state-of-the-art" survey was conducted at the initiation of this program. This survey included a comprehensive review of the literature, a complete patent search, and an analysis of sources of material that could have potential use as modifiers for sulfur.

Chemically, sulfur is a very reactive element similar to oxygen and enters into reactions with many other elements and compounds. The reaction products number in the thousands. Very few of the reaction products are polymer or plastic-like materials. In most instances, books and papers on sulfur chemistry revealed very little information on the physical properties of the reaction products. "Sulfur-Containing Polymers" by E. J. Goethals (Inst. Org. Chem., Rijsuniv, Gent, Ghent, Belt.) *Topics in Sulfur Chemistry*, 1977, 3, 1-61, is one of the best reference sources uncovered in this work. No information was found in the literature search that revealed where the use of small quantities of additives of any type with sulfur would yield products of liquid or extremely plastic-like characteristics as considered needed for pavement binders.

The patent search yielded 31 patents which are listed below.

Patent No.	*Title*
3,965,067	Method for Plasticizing Sulfur
3,823,019	Mine Wall Coating
3,734,753	Plasticized Sulfur Compositions
3,721,578	Plasticized Sulfur, Asphalt Impregnated Fabric
3,674,525	Plasticized Sulfur Compositions
3,631,158	New and Useful Sulfur Compositions
3,619,258	Modification of Patent No. 3,721,578 above
3,560,451	Plastic and Nonflammable Sulfur Composition
3,510,329	New Sulfur Compositions
3,472,811	Sulfur Containing Compositions
3,465,064	Plasticized Sulfur Containing an Olefine
3,459,717	Sulfur-Based Plastic Composition
3,455,328	Sulfur Containing Elastomers
3,453,126	Novel Polymercaptan Sulfur Compositions
3,437,498	Novel Dialkeynl Polysulfide-Sulfur Compositions
3,453,125	Plasticized Sulfur Compositions
3,615,748	Process for Preparing Plasticized Sulfur Road Markings
3,427,292	Modified Sulfur
3,421,911	Plasticizer for Sulfur Road Marking Material
3,384,609	Plasticized Sulfur
3,371,072	Sulfur Resins
3,352,837	Sulfur-Containing Resinous Products
3,316,115	Marking Composition
3,290,266	Compositions Containing Elemental Sulfur
3,047,543	Sulfur-Containing Heat Resistant Resins
3,020,252	Road Marker Materials
2,799,593	Jointing Composition
2,707,685	Sulfur Composition
2,450,771	Plastic Sulfur Vulcanizing Agent
2,284,432	Plastic
2,280,301	Sulfur Compositions

Several of the patents listed above were issued to the individuals working on this project. Many of the reactions or processes described in these patents have been tried in this laboratory in the past. After careful study, it was concluded that none of the products or processes described in the patents were suitable for use in this program for one or more of the following reasons:

1. They did not yield products that were plastic of the degree required for the subject application.
2. They involved the use of sophisticated chemical products and reactions that were too complex for consideration in the subject application.
3. They involved the use of chemicals or modifiers that were of limited present and future availability.
4. They involved the use of chemicals that were too costly to be considered for the subject application.
5. They involved the use of proprietary single source chemicals and/or processes whose use would be at the discretion of the owner of the patent.

Nowhere in the literature or patent search was there found any reference to products or processes that would modify sulfur to the degree sought on this project, or was there any reference to modifying sulfur to perform as a binder for the preparation of flexible pavements.

All of the information uncovered in the literature and patent search was assembled, documented, and presented to the Sponsor and the consulting team, who agreed with the conclusion of the project investigators that whatever was to be used on this project would have to be developed on this project.

It was further concluded that the principal source industries from which modifiers would be sought would be:

1. Coal
2. Naval Stores
3. Mining
4. Agricultural
5. Petroleum

Since 1959, SwRI has had an active program in sulfur product development. Numerous chemical additives have been evaluated as property modifiers for elemental sulfur. During the course of this work, some general observations have been made regarding potential modifiers for sulfur—particularly when reacted with sulfur under atmospheric conditions. Straight chain paraffinic type materials are not miscible with sulfur, nor do they react to produce a material with desirable properties. The unsaturated straight chain materials are not much better until the higher boiling point materials are used. Cyclic and aromatic materials are more soluble in sulfur, but no reaction or permanent modifying properties are obtained unless there are unsaturated bonds present. For example, chlorinated naphthalene or benzene and xylene will be soluble in sulfur, but no reactions occur which modify the sulfur properties. Cyclooctene or styrene monomer, however, will react with sulfur to produce an end product different than elemental sulfur.

The rationale at the initiation of the program was to screen a large number of low-cost additives first. If this was unsuccessful then more expensive materials would have been screened, and as a last resort, laboratory manufacture of modifiers would have been attempted. From past experience it was known that for every percent of modifiers that cost $1.00 per pound, the resultant cost of the final product would be increased by 1 cent above the sulfur cost. For example, if sulfur were 3 cents per pound and 10% of a modifier costing $1.00 per pound were used, the resultant modified sulfur cost would be approximately $0.13 per pound or $260 per ton. Thus, any significant amount of expensive modifier would drastically affect material costs.

The arbitrary decision was made to first screen materials with a cost of 40 cents per pound or less. It was known that numerous potential materials fell within this cost restriction. Generally speaking, the availability of any such low-cost additive was good, as opposed to the higher priced specialty chemicals, and this was desirable.

In addition, the decision was also made to not use hologenated compounds or the poisonous inorganic modifiers such as phosphorus or arsenic.

In December 1976, an interim report was submitted to the Sponsor covering the findings of the literature search in detail.

LABORATORY WORK (Tasks B-F)

The principal objective of this program was to develop a system to modify sulfur so that it would serve as a replacement for asphalt and Portland cement. Studies of mixtures of these materials with aggregates and the measurement of their properties as related to their use in pavements was not considered initially as a portion of this effort. As the laboratory work proceeded, a system to modify sulfur was expeditiously developed and it became not only desirable but necessary to prepare mixtures of the developed binder materials with aggregates and measure their properties. One single optimized gradation of limestone was selected and all testing used this gradation with 6% by weight of each SULPHLEX formulation. The properties of the resultant concrete were then compared against the same gradation with 6% by weight of either an AC-10 or AC-20 asphalt as the binder. In this way the SULPHLEX binders were compared in performance against the asphaltic binders. In addition to determining mechanical properties, it was also possible to determine such information as the stripping characteristics that SULPHLEX exhibited with different aggregate types and the types of formula modifications necessary to achieve the types of properties deemed most desirable for pavement applications.

Formulation of SULPHLEX

From the beginning it was obvious that if sulfur were to be used as a pavement binder, it would have to be modified to exhibit more plastic characteristics. The term plasticized sulfur is clouded by the fact that it has different meanings to different people. By definition a plasticizer is normally thought of as an additive that, when added to a resin, imparts flexibility, workability, and stretchability. There is no qualification as to whether the mechanism is one derived as the result of a physical change, a chemical reaction, or a simple mechanical change. Strictly speaking, elemental sulfur fails to qualify as a resin. On the other hand, elemental sulfur, when heated to above its transition temperature of 160° C and rapidly quenched at 20° C, exhibits a plastic characteristic that everyone is familiar with, hence the term "plastic sulfur". Unfortunately, if the material is allowed to return to room temperature, it quickly hardens with the formation of orthorhombic S_8 sulfur crystals. Evidence exists that above 160° C molten sulfur consists of a mixture of S_8 rings and S_x chains where the value of x can be very large. Different investigators have different opinions as to what exactly occurs. Some suggest that the S_x chains plasticize the S_8 rings. Others suggest that the S_8 rings plasticize the S_x chains. In either case, the mechanism of "plastic sulfur" is brought about by physical change that does not lend itself to practical application in the preparation of binders for paving.

What remains then for consideration is the conversion of sulfur to a plastic by a chemical reaction, a mechanical change, or a combination of these. The ability to produce useful, low-cost plastics from sulfur has thus far eluded mankind, as evidenced by the fact that one does not find such products in the marketplace. In the laboratory it is possible to produce plastic sulfur compositions in accordance with the state-of-the-art as set forth in the patent and open literature, but these products are still relatively hard and brittle at room temperature and more closely resemble sulfur than they do plastics. None give products at room temperature having the viscosity, penetration, and other characteristics similar to asphalt.

Most systems devised to modify sulfur are based on the use of one additive. The SULPHLEX system is based on the reaction of multiple additives with elemental sulfur. Once reacted, all of the SULPHLEX formulations resemble asphalt and are handled like asphalt. Once they are in place, the pavement either continues to exhibit the characteristics of a flexible pavement, or with time, it assumes the characteristics of a rigid pavement. This is controlled by the amount and type of additives employed.

The method of addition of the chemical additives to the sulfur is important in that certain of the additives react exothermically with sulfur, i.e., on reacting they liberate heat. Thus, if the reaction is carried out at too high a temperature, the reaction proceeds too rapidly, and control over the reaction can be lost.

Screening of Materials (Task B)

In screening the chemicals, the initial experiments used as much as 30% by weight of a single modifier and 70% by weight sulfur. The resultant product was allowed to solidify and was observed for up to three days, although in each instance, the resultant formulation solidified into a hard, rigid material, usually within the first 24 hours after being cooled.

Combinations of two modifiers were then pursued, with total additives being as much as 30% by weight and the remainder being sulfur. This approach was more successful in that several formulations were prepared that had supercooling tendencies; however, for the most part, the resultant products reverted to hard, brittle materials.

Combinations of three or more modifiers were then investigated, and this technique yielded several formulations that appeared to have prolonged stability as an asphalt-like material.

The second stage in the chemical development was to select the more promising formulations and measure penetration, ductility, and softening point and compare against an AC-10 and an AC-20 asphalt control. Modifications to the formulations were made, and the ratios of the modifiers were adjusted as necessary in order to produce materials with a full range of penetration, ductility, and softening points. The more promising formulations were then evaluated as a function of time and temperature.

Of unusual importance in the subject application was the use of modifiers whose cost effectiveness was such that they did not increase the cost of the final product to a level where it was too costly for consideration as a binder for paving. During the course of this work, the vapors, odors, and gaseous reaction products were observed for each experiment. Particular attention was paid to any H_2S or SO_2 that might have been generated during the reaction. The more promising formulation developed did not generate any detectable H_2S or SO_2.

The procedure developed in the laboratory for 200-1000 g batches was to heat the sulfur to 150° C in an open beaker. All of the modifiers were first blended and then added to the molten sulfur. In these smaller batches, the temperature was maintained between 150-170° C by removing the heat source if the temperature became too high and replacing the heat source if the temperature dropped. Depending on the specific formulation, reaction times could vary from 1-3 hours. It was found that when 1% or less of a previously reacted SULPHLEX formulation was added to a new batch, autocatalysis occurred and the reaction time could be reduced to less than one hour in these laboratory size batches.

Screening of Special Additives (Task C)

The materials developed during the program did not require any special additives in order to achieve desirable properties. The modifiers that were ultimately selected as the most promising, for example, produced a fire retarded material. Properties such as viscosity, wetting characteristics, and color could all be adjusted by the type or quantity of modifiers used.

Investigation of Plasticizer Homologues and Reaction Parameters (Task D)

During the course of this program, over 450 different formulations were prepared using combinations of 80 different modifiers. All work was conducted in open vessels.* Considering combinations of two, three, or more modifiers, many more possibilities are possible. Twenty-one of the more promising formulations are listed in Table 1.

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*In preparation for the experimental roadway work, the production of SULPHLEX binders had to be scaled-up. The available reaction vessels were large impregnation vats 4 ft x 4 ft x 8 ft (1.22 m x 1.22 m x 2.4 m). The procedure developed for making SULPHLEX formulations in these large vessels necessitated good temperature control to insure that the material did not overheat, which could have resulted

TABLE 1. TWENTY-ONE PROMISING FORMULATIONS

No. 233

70% Sulfur (S)
12% Cyclodiene Dimer Concentrate (CDC)
10% Dipentene (DP)
8% Vinyl toluene (VT)

No. 39

70% S
12% Dicyclopentadiene (DCPD)
10% DP
8% Creosote

No. 330

70% S
12% Aromatic tar
10% DP
8% VT

No. 126

61% S
13% CDC
13% VT
13% Coal Tar (CT)

No. 305

70% S
12% Methylcyclopentadiene (MCPD)
10% DP
8% VT

No. 216

70% S
12% CDC
12% Asphalt
6% Tall Oil Pitch

No. 230

70% S
15% CDC
15% DP

No. 312

70% S
12% 1,7 Octadiene
10% DP
8% VT

No. 200

70% S
10% Aromatic tar
10% CDC
10% Styrene

No. 334

70% S
12% Unsaturated Aliphatics
8% VT
10% DP

No. 314

70% S
12% Vinylcyclohexene-1
10% DP
8% VT

No. 163 (Mod)

70% S
15% DCPD
15% Pinene

No. 344

70% S
12% Poly DCPD
10% DP
8% VT

No. 345

70% S
15% CDC
15% Pinene

No. 355

70% S
12% CDC
18% Dipentene-Dimercaptan

No. 433

70% S
10% CDC
3% DCPD
10% Tall Oil Pitch
7% DP

No. 398

70% S
12% DCPD
18% Indene

No. 381

70% S
12% Phosphorus Pentasulfide
8% VT
10% DP

No. 430

66% S
17% Hydroxyl terminated butadiene Polymers
17% DP

No. 443

65% S
15% CDC
15% Tall Oil Pitch
5% DP

No. 449

70% S
15% CDC
15% Tert-Butylstyrene

In addition, by retaining the same ratio of modifiers but simply increasing the sulfur content, rigid formulations can be prepared from the flexible and intermediate formulation. The four formulations which have been characterized in detail are the three used in the experimental roadway, formulations No. 233, No. 126, and No. 230, as well as later developed formulation No. 433.

The properties of formulations No. 233 and No. 433 are similar to an AC-20 asphalt. The properties of No. 230 are initially similar to asphalt, but with time, No. 230 hardens to give Portland cement concrete-like properties in pavements. Formulation No. 126 has properties intermediate between these two extremes.

In addition, the cost and availability of the modifiers in these four formulations makes them the most promising for immediate scale-up. Some of the remaining formulations may find specialized applications, but the costs will be greater because of higher prices for the modifiers.

The chemistry of SULPHLEX is complex. In simple terms, the desired SULPHLEX products are obtained when a cross-linking or gelling agent is used in combination with one or more linear modifiers. Formulation No. 233 is a typical example. If the vinyl toluene is left out completely, a formulation similar to No. 230 is produced, which is a rigid product. Likewise if the dipentene is left out, the resulting product is also rigid. The combination of the vinyl toluene and dipentene in conjunction with the cyclodiene dimer concentrate, however, yields an asphalt-like material. If only the cyclodiene dimer concentrate is added at a level greater than 5%, the resultant product will gel in the container and cannot be poured or otherwise handled. The presence of the vinyl toluene and/or dipentene thus prevents this gelling phenomena as well. That is why the order of addition is important. The modifiers are either blended together and then added, or else the cyclodiene dimer is added last so that the gelling is avoided.

The parameters of time, temperature, and pressure were also investigated during the course of the project.

The procedure developed in the laboratory for 200-1000 g batches was to heat the sulfur to 150° C in an open beaker. All of the modifiers were first blended, and then added to the molten sulfur. In these smaller batches, the temperature was maintained between 150-170° C by removing the heat source if the temperature became too high and replacing the heat source if the temperature dropped. Depending on the specific formulation, reaction times could vary from 1-3 hours. Numerous attempts were made to produce a similar product by keeping the reaction temperature at 140° C, but the resultant products always reverted to a hard, brittle material within a few days. Reaction times as long as 24 hours were used but the resultant product was never satisfactory. The product obtained by reacting at 140° C never produced a comparable material to one reacted at 150° C.

It was also found that the reaction time could be reduced substantially by the addition of 1% or less of previously reacted SULPHLEX formulation. This autocatalysis can best be described by a typical reaction involving formulation No. 233. In one experiment, 300 g of formulation No. 233 was prepared and heated to 150° C. Half of the material was poured into a clean beaker and approximately 1 g of previously made SULPHLEX was added. The temperature climbed immediately to 210° C, and within 30 minutes, the material was reacted to produce a material with a 7-day penetration of 75. The rest of the formulation in the second beaker (without the addition of catalyst) was reacted for two hours and the temperature never went above 165° C. It had a 7-day penetration of 6.

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in boil-over of the material. Since there was no means of cooling these vats, temperature control had to be accomplished by careful stepwise addition of the plasticizers and watching for any temperature rise. The procedure finally adopted was to heat the 6000 lb (2722 Kg) of sulfur to 150° C, add 10 gallons (.038 m^3) of each modifier, and watch the temperature. When the temperature of the material returned to 150° C, the procedure was repeated until all the modifiers were added. This procedure took 8-12 hours to accomplish depending on the formulation. The material was then stored at a temperature of 130-140° C until it was used.

The parameter of pressure was not pursued until near the end of the project. The anticipation of having to produce a total of 51,000 lb (23,000 Kg) of SULPHLEX in the large open vats for the experimental roadway necessitated developing procedures for manufacture at atmospheric conditions. Secondly, the fact that there is a highly exothermic reaction in the preparation of SULPHLEX could generate uncontrollable temperature and pressure in a pressurized vessel. Recent experiments with 1000-1300 lb (454-590 Kg) batches indicate that a vented reactor, which allows for the condensation of the volatile fraction of the modifiers, allows for a rapid, controllable reaction with a minimum of fumes and vapors. The condensed products are added back to the batch, although they are usually less than a quart (or a liter) of material out of a total plasticizer volume of 50 gallons (192 l).

Properties of SULPHLEX (Task E)

The properties of SULPHLEX have been determined from tests originally developed for asphalts and tars. It is convenient to use these tests, not only because they have been developed and published as standards, but they also give an indication of the suitability of a material for use as a binder in roadway paving mixes, which is the primary use intended for SULPHLEX. A blind, outright application of these asphalt tests to SULPHLEX should not be made because SULPHLEX differs from asphalt in several ways. For instance, some SULPHLEX formulations show a hardening or setting-up characteristic about 24 hours after preparation. (See formulation No. 230 in Figure 4.) The tests for penetration and viscosity would show values lower than would be expected for asphalt, but an aggregate mix with this particular formulation would be very stable on a roadway.

The property undergoing the greatest change in the modification of sulfur to produce SULPHLEX is the viscosity. Figure 2 on the following page shows a comparison of the viscosity curve of elemental sulfur with typical 60 PEN and 300 PEN type asphalts. The curve for one particular SULPHLEX formulation is also shown. The similarity between it and the curves for asphalt is noteworthy. Figure 3 is a full range viscosity graph showing a comparison of typical asphalt viscosities with the viscosity of SULPHLEX after exposure to the air at ambient temperature for one year. Of interest is the temperature for best mixing with aggregates. SULPHLEX formulations Nos. 233 and 433 heated to only 200° F (93° C) have a viscosity value low enough to provide good mixing, all other factors being equal.

There is a definite tendency for SULPHLEX to harden with age. The type of sulfur modifiers and the amount of these modifiers used to make the SULPHLEX formulation determine the initial penetration value and the rate of penetration loss. (See Figure 4.) If in formulation No. 233, 35% of the modifiers were used rather than 30%, a penetration value as high as 75 was obtained after a year, and there was every indication that several more years would see very little drop in this value.

Formulations classified as "rigid" type can be made soft enough to mix well and be placed with conventional paving equipment, but the mixtures will harden within a week on the roadway to provide a rigid type of pavement. Formulation No. 230 in Figure 4 is an illustration of this phenomenon.

Figure 5 shows the relationship of temperature with penetration for 7-day-old and 6-month-old SULPHLEX No. 233, which is a flexible formulation, and for No. 230, which is a rigid formulation.

Figure 6 shows how the amount of modifiers affects the strength of SULPHLEX. To permanently modify sulfur to the degree which will bring about typical asphaltic characteristics, it appears necessary to add approximately 30 to 35% modifiers to approximately 65 to 70% sulfur when open reaction vessels are used. As time goes by, more effective and possibly more economical modifiers may be developed, and the use of pressure or closed, vented vessels will undoubtedly change the values shown in Figure 6.

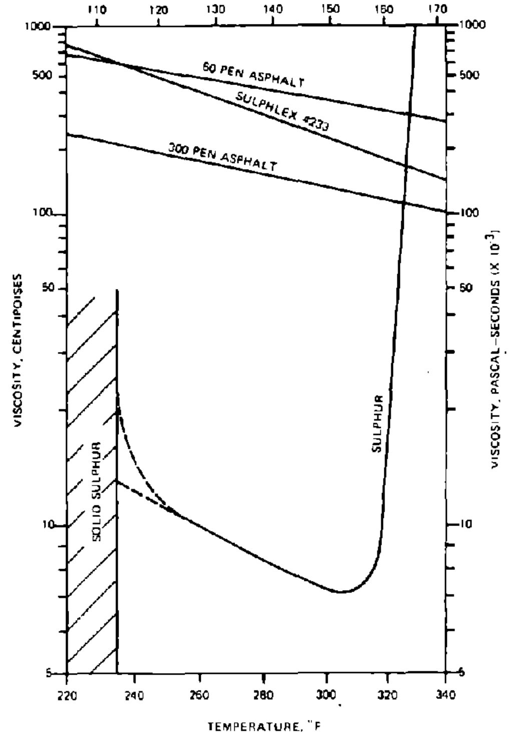


Figure 2. Viscosity-temperature relationships for asphalts and SULPHLEX.

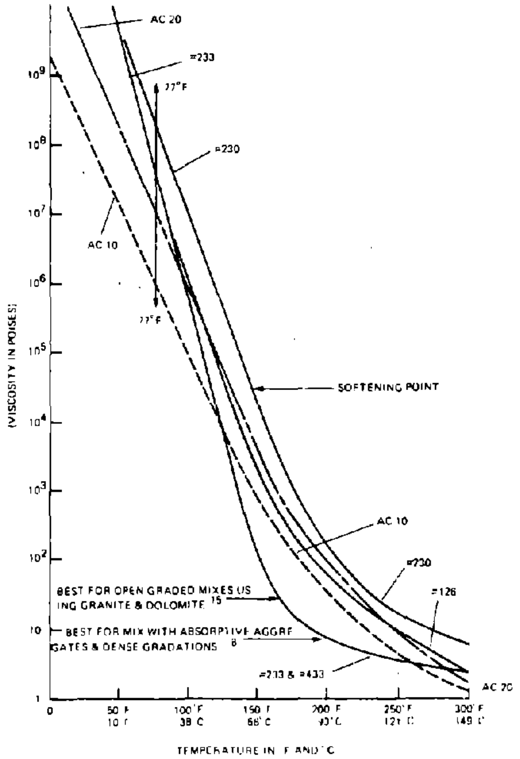


Figure 3. Viscosity of one-year-old binders.

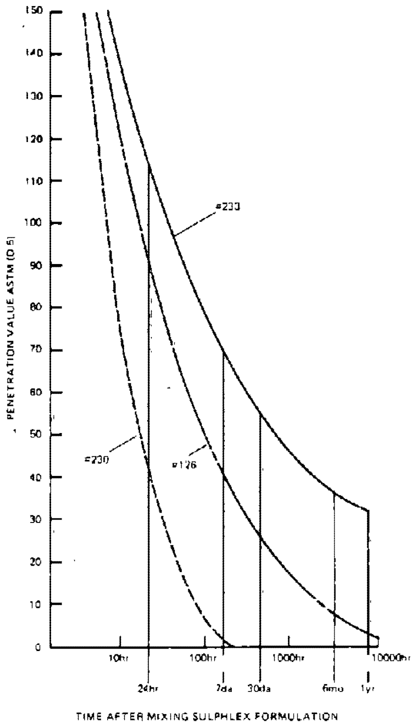


Figure 4. Characterisitcs of SULPHLEX aging data based on averages.

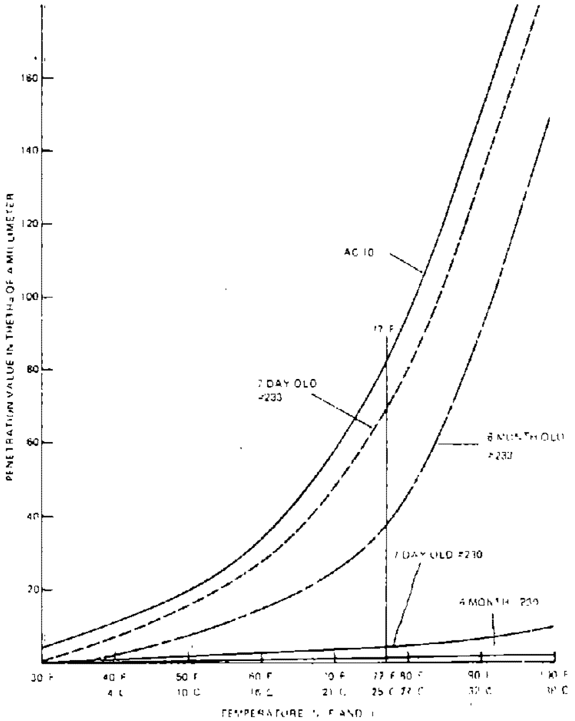


Figure 5. Variation of penetration with temperature for a flexible type and a rigid type SULPHLEX.

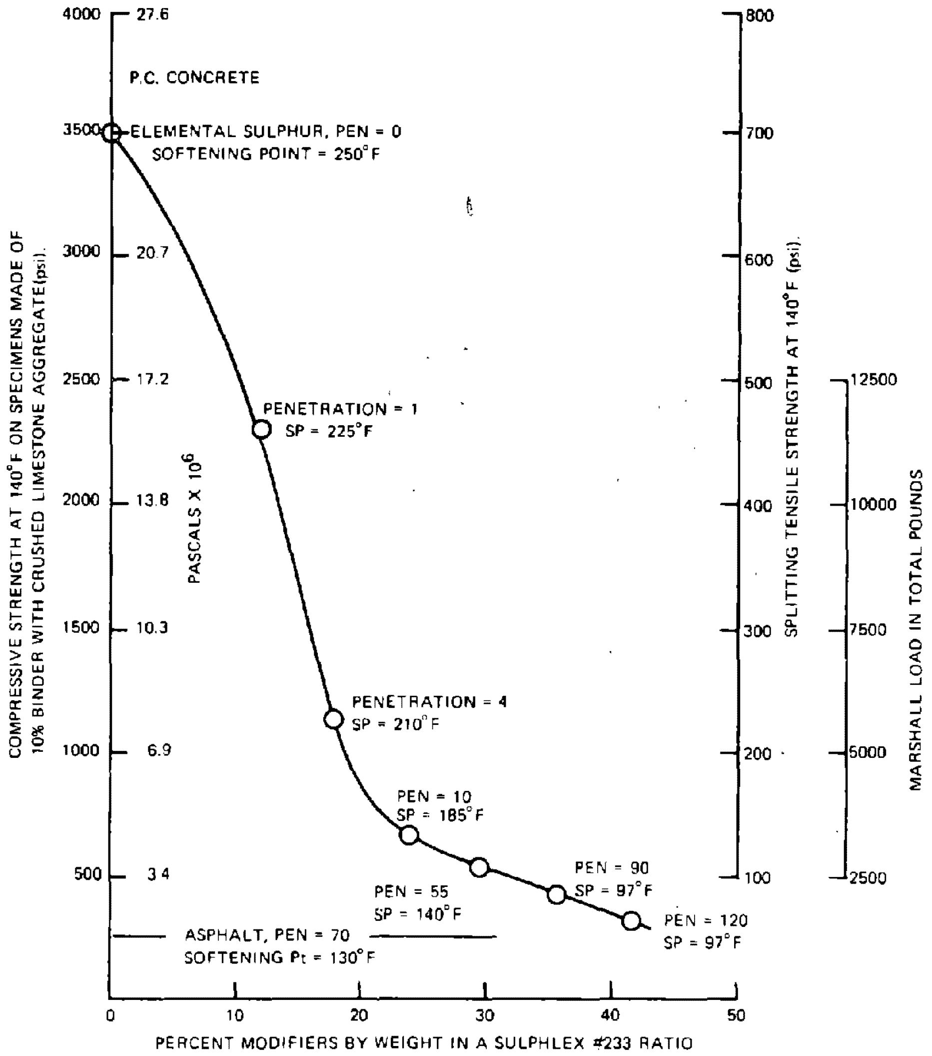


Figure 6. Variation of strength with the percentage of modifiers used to make SULPHLEX.

During the development of SULPHLEX, the results of two asphalt tests, ASTM D5 for penetration, and ASTM D36 for the softening point, became the primary basis for an initial judgment of typical asphaltic properties. Formulations that showed penetration and softening point values similar to AC-10 and AC-20 were further evaluated by means of the standard ASTM Tests for ductility, viscosity, flash point, tensile strength, compressive strength, toughness, thermal expansion, electrical and thermal conductivity, health hazard, pot life, specific gravity, thin film oven, ultraviolet radiation, biological attack, and various tests on mixes of SULPHLEX with certain aggregates. A summation of the test results is found in Tables 2-3. One of the tests that may be unfamiliar to some is the caffeine test, which is an indication of the potential health hazard of the SULPHLEX formulations. The Esso "Caffeine Number" method is a physical-chemical procedure for predicting the carcinogenic potency of certain high boiling petroleum products. As reference points, white mineral oil has a caffeine number (C^n) of 0.003 and a predicted tumor potency of 10 and is considered a relatively safe material; coal tar, with a C^n of 15.5 and a predicted tumor potency of 123, is considered a relatively hazardous material.

TABLE 2. COMPOSITION AND SUMMARY OF PHYSICAL TESTS ON SULPHLEX BINDERS
(English System)

Composition		No. 230			No. 126			No. 233			No. 433			AC-20		
Sulfur		70%			61%			70%			70%			—		
Dicyclopentadiene		15			13			12			13			—		
Dipentene		15			—			10			10			—		
Vinyl toluene		—			13			8			—			—		
Coal Tar		—			13			—			—			—		
Tall Oil Pitch		—			—			—			10			—		
AC-20		—			—			—			—			100%		
PHYSICAL TEST	°F	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo
Penetration, ASTM(D5) Always tenths of a mm	77	40	5	1	90	40	10	110	70	35	110	70	35	55	55	55
Softening Pt, ASTM(D36) Degrees F		125° F	158° F	200	105	158° F	190	100	118° F	130	100	118° F	130	131	131° F	131
Ductility, ASTM(D113)	-20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Always in cm	77	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +
Viscosity (Brookfield) Poises	275	9p	10p	10p	6p	7p	7p	2p	3p	3p	2p	3p	3p	5p	5p	5p
Flash Point, ASTM(D92)° F		372	374	374	352	356	356	352	356	356	352	356	356	500	500	500
Tensile Strength, ASTM	-20	250	350	400	200	300	300	200	300	300	—	300	—	250	250	250
(C496) lb per sq in.	77	10	20	25	10	20	25	0	2	3	—	2	—	2	2	2
(Approximate values based on single specimen tests.)	140	0	1	2	0	0	1	0	0	0	—	0	—	0	0	0
Compressive strength,	-20	2000	2430	2500	1900	2200	2300	1800	1930	2000	—	2000	—	1700	1710	1700
on 2 in. cubes in	77	10	28	40	10	14			1			1			1	
psi (approximate values based on single specimen tests.)	140	0	0	1	0	0	1	0	0	1		0		0	0	0
Toughness, height of	-20	3			3			12			12			6		
fall of 1 lb weight	77	16			18			36			36			12		
to make specimen shatter, in in.	140	no shatter			no shatter			no shatter			no shatter			no shatter		
Thermal Expansion, per °F		3×10^{-5}			3×10^{-4}			3×10^{-4}			3×10^{-4}			3×10^{-4}		
Elect Cond (Res in Ohm in.)	77	$3 \times 10^{11+}$			$3 \times 10^{11+}$			$3 \times 10^{11+}$			$3 \times 10^{11+}$			3×10^{15}		
Therm Conductivity in/hr/ft²/°F)	77	5.2			5.2			5.2			5.2			5.2		
Health Hazard																
a. (Caffeine)		0.085			1.58			0.098						0.051		
b. Predicted Tumor Potency		19			78			21			43			10.1		
Pot Life	140	1 yr +			1 yr +			1 yr +			1 yr +			1 yr +		
SP Gravity, ASTM (D71)	-20	1.58			1.45			1.56			1.48			1.04		
	77	1.57			1.43			1.54			1.47			1.02		
	140	1.52			1.40			1.48			1.45			1.00		
Thin Film Oven (ASTM 1754)	375	5% Loss 0.5 Ratio			4% Loss 0.6 Ratio			5% Loss 0.5 Ratio			4% Loss 0.6 Ratio			0% Loss 0.6 Ratio		

Ultraviolet (1 year) Good resistance after 1 year's exposure in road.

Biological Attack Specimens moved and lost by city personnel when lift station was remodeled

TABLE 3. COMPOSITION AND SUMMARY OF PHYSICAL TESTS ON SULPHLEX BINDERS

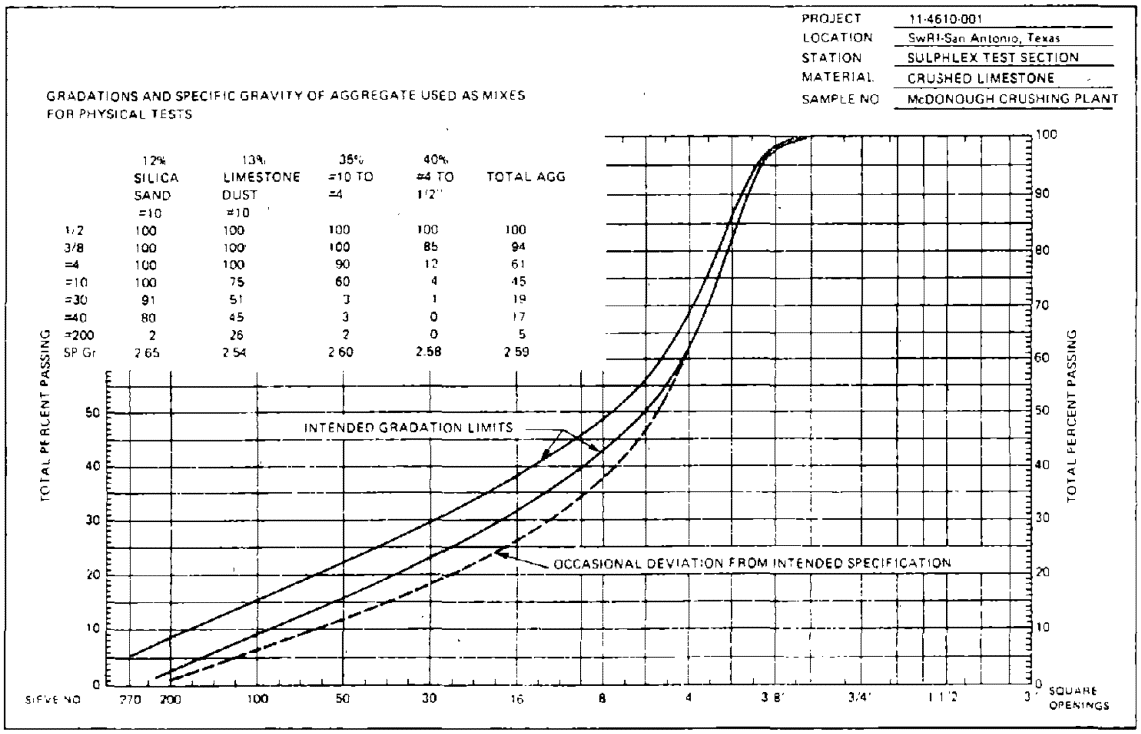
(Metric System)

Composition			No. 230			No. 126			No. 233			No. 433			AC-20	
Sulfur			70%			61%			70%			70%			—	
Dicyclopentadiene			15			13			12			13			—	
Dipentene			15			—			10			10			—	
Vinyl toluene			—			13			8			—			—	
Coal Tar			—			13			—			—			—	
Tall Oil Pitch			—			—			—			10			—	
AC-20			—			—			—			—			100%	
PHYSICAL TEST	°C	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo
Penetration, ASTM (D5)	25	40	5	1	90	40	10	110	70	35	110	70	35	55	55	55
Softening Pt, ASTM (D36)			70° C			70° C			48° C			48° C			55° C	
Ductility, ASTM (D113)	-29	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	25	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +	100 +
Viscosity (Brookfield)	135	9p	10p	10p	6p	7p	7p	2p	3p	3p	2p	3p	3p	5p	5p	5p
Flash Point, ASTM (D92)° C		189	190	190	178	180	180	178	180	180	178	180	180	260	260	260
Tensile Strength, ASTM	-29	17	25	28	14	21	21	14	21	21	—	21	—	18	18	18
(C496) kg per sq cm	25	0.7	1.5	1.7	0.7	1.4	1.7	0	0.15	.2	—	0.15	—	0.15	0.15	0 15
(approximate values based on single specimen tests.)	60	0	0.07	0.14	0	0	.07	0	0	0	—	0	—	0	0	0
Compressive strength,	-29	140	170	175	133	154	160	126	135	140	—	140	—	120	120	120
on 5 cm cubes in Kg/cm^2	25	0.7	2	2.8	0 7	1	2.1	0	0.1	0.2	—	0.1	—	0.1	0.1	0.1
(approximate values based on single specimen tests.)	60	0	0	0	0	0	0	0	0	0	—	0	—	0	0	0
Toughness, height of	-29		7			8			30			30			15	
fall of 454 gr weight	25		40			46			91			91			30	
to make specimen shatter, in cm	60		no shatter			no shatter			no shatter			no shatter			no shatter	
Thermal Expansion, per °C			6×10^{-5}			5×10^{-4}			6×10^{-4}			6×10^{-4}			6×10^{-4}	
Elect Cond (Res in Ohm cm)	25		10^{11+}			10^{11+}			10^{11+}			10^{11+}			10^{13+}	
Therm Conductivity (W/m/K)	25		0.7			0.7			0.7			0.7			0.7	
Health Hazard (Caffeine)			19			78			21			43			17	
Pot Life at 60°C	60		1 yr			1 yr			1 yr			1 yr			1 yr	
Sp Gravity, ASTM (D71)	-29		1.58			1.45			1.56			1.48			1.04	
	25		1.57			1.43			1.54			1.47			1.02	
	60		1.52			1.40			1 48			1.45			1.00	
Thin Film Oven	163		5% Loss			4% Loss			5% Loss			4% Loss			0% Loss	
(ASTM 1754)			0.5 Ratio			0.6 Ratio			0.5 Ratio			0.6 Ratio			0.6 Ratio	
Ultraviolet (2 year)																
Biological Attack																

Properties of SULPHLEX Mixes (Task F)

Certain formulations showed such desirable engineering properties early in the program that allowance was made to carry the research a step further by investigating the properties of some of the formulations *in mixes* with aggregate. This procedure appeared necessary because similarity or dissimilarity of the physical properties of the modified sulfur with asphalt does not necessarily mean that the new material will function well or poorly with aggregates in a roadway. It appeared that the only way to determine the performance of the new SULPHLEX binders with certainty was to mix them with aggregates and perform appropriate tests.

For purposes of this study, one well graded limestone aggregate native to the San Antonio area was selected for all of the mixes used throughout the program. The gradation selected is shown in Figure 7. The optimum binder content was determined using both AC-10 and AC-20 asphalts from a plot of Marshall test load values versus percentage of binder. The optimum binder content using SULPHLEX formulation No. 233 was determined in the same manner and the results are shown in Figure 8. There was concern at the beginning of the testing phase that since the specific gravity of the modified sulfur binder was nearly 1.6, it would take approximately 60% more sulfur binder by weight to provide the *same* volume of binder in the mix. However, as Figure 8 shows, the optimum binder content based on stability for the SULPHLEX mixes is close to the optimum binder content for asphalt mixes. On this basis, SULPHLEX can be substituted for asphalt pound for pound with limestone aggregates; however, less volume of SULPHLEX is used. The reason for the high strength of low-percentage binder mixes may be the lower viscosity of SULPHLEX at the usual mixing temperature of 250° F (121° C), as discussed earlier. The standard procedure was to use 6% by weight of SULPHLEX binder in all of the mixes and then always compare the resultant properties against asphalt control mixes made with 6% by weight asphalt. SULPHLEX was simply substituted for asphalt on a 1 to 1 weight basis. Marshall tests, unconfined compression tests, split tensile tests, and modulus of resilience tests showed excellent properties for a number of the SULPHLEX formulations with limestone aggregate. Figure 9 illustrates that SULPHLEX as a binder has the potential of producing concretes that can span the range from flexible materials to the more rigid concretes. The numbers identifying each curve are specimen identification numbers from the project notebook.


PROJECT 11-4610-001
LOCATION SwRI-San Antonio, Texas
STATION SULPHLEX TEST SECTION
MATERIAL CRUSHED LIMESTONE
SAMPLE NO McDONOUGH CRUSHING PLANT

GRADATIONS AND SPECIFIC GRAVITY OF AGGREGATE USED AS MIXES FOR PHYSICAL TESTS

	12% SILICA SAND #10	13% LIMESTONE DUST #10	35% #10 TO #4	40% #4 TO 1/2"	TOTAL AGG
1/2	100	100	100	100	100
3/8	100	100	100	85	94
#4	100	100	90	12	61
#10	100	75	60	4	45
#30	91	51	3	1	19
#40	80	45	3	0	17
#200	2	26	2	0	5
SP Gr	2.65	2.54	2.60	2.58	2.59

Figure 7. Gradation chart.

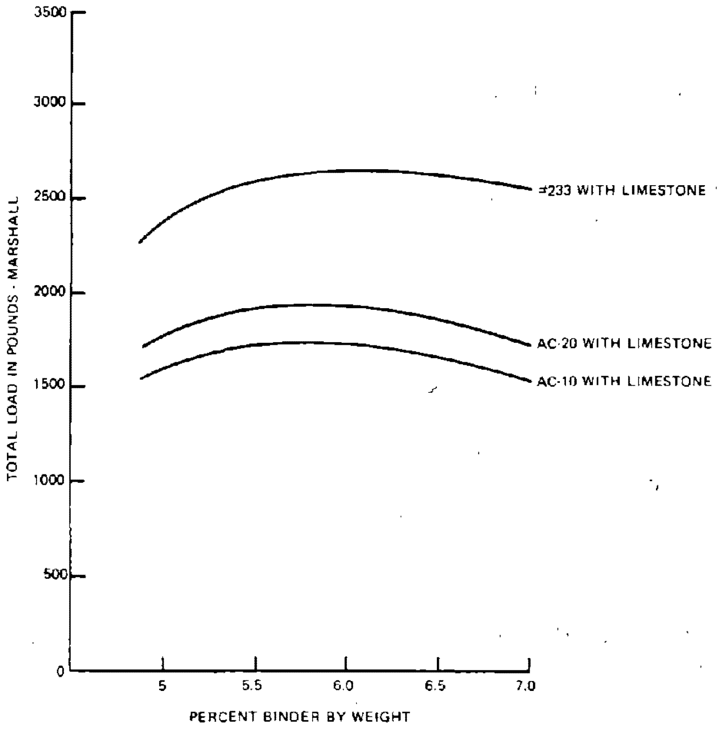


Figure 8. Optimum binder content using the Marshall Stability Tester.

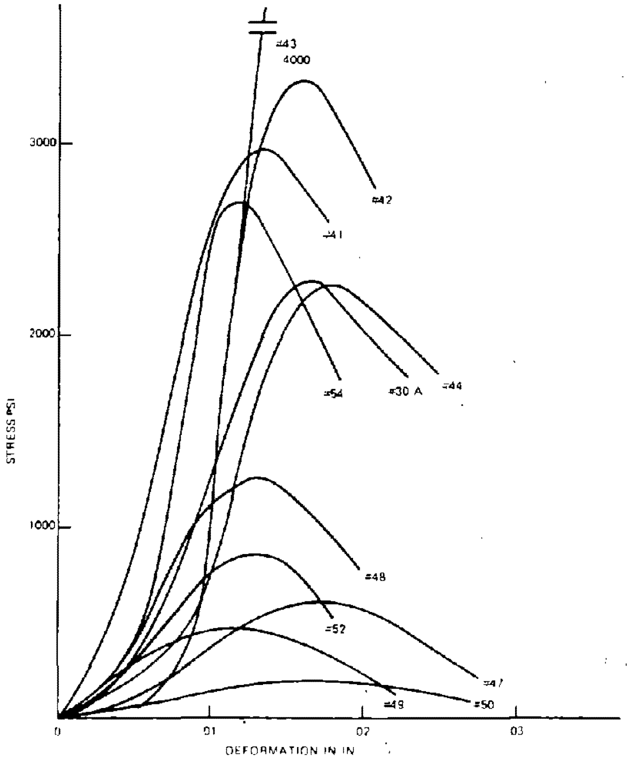


Figure 9. Stress-deformation curves for selected SULPHLEX concretes.

The fact that a lesser volume of SULPHLEX, compared to asphalt, is used in the prepartion of the mixes would indicate that the SULPHLEX films around the aggregate are thinner than the asphalt films. This could be a disadvantage when attempting to obtain high stability with a water saturated mix or when working with aggregates that have poor stripping characteristics. Two such aggregates were investigated. One was a basalt from Oregon and the second was a river gravel from Arizona. Table 4 summarizes the physical test results for both the limestone and the stripping type aggregates. It will be noted that the limestone withstood over a hundred freeze-thaw cycles when mixed with all three SULPHLEX formulations and also with the AC-20. On the other hand, the stripping type of aggregates withstood only about 60 freeze-thaw cycles when mixed with 6% SULPHLEX, and they withstood 60 to 71 cycles when mixed with 6% AC-20. Apparently, it is the type of aggregate that determines the amount of stripping to the greatest extent, and neither 6% SULPHLEX nor asphalt will prevent stripping if the aggregate is so inclined.

Emulsification, Rejuvenation, and Additional Experimentation

Three additional areas were pursued to a very limited extent. Although they fell outside the scope of the subject program, once promising formulations were developed, these three areas were logical applications for SULPHLEX in the pavement applications area.

It was demonstrated that SULPHLEX formulations No. 126 and No. 233 could be successfully emulsified, and the emulsions were used as tack coats for two small patches installed on the Institute grounds in August and December 1977. In December 1977, it was demonstrated that the emulsion could be spray applied. Several other flexible formulations were readily emulsified, and some are still emulsified after having been exposed in open containers for two years. Two commercial asphalt emulsifying agents were investigated, but neither were successful in emulsifying any of the SULPHLEX formulations. One promising system employed saponifying oleic acid with caustic as the emulsifying agent. These formulations were emulsified by high-speed laboratory mixers and did not require the use of colloid mills.

The second area investigated was the use of SULPHLEX as a rejuvenator for old asphalt pavements. It was found that when 2-3% by weight of SULPHLEX was added to an old, pulverized asphaltic pavement material in the laboratory, the test specimens showed approximately a 3000 lb (1360 kg) load in the Marshall test, and 500 psi (35 kg/cm^2) unconfined compressive strength on saturated cylinders at 140° F (60° C). It appears that SUPLHLEX could be used very satisfactorily as an old pavement rejuvenator.

The third area of interest was the use of different aggregate types. From previous experience*, it was known that elemental sulfur yielded different mechanical properties with granite aggregates than with limestone aggregates. In addition, on this project, it appeared that crushed limestone mixes were showing considerably more strength with SULPHLEX than with asphalt. The same granite material from Marble Falls, Texas, used in the earlier studies, as well as granite from Golden, Colorado, were obtained and used in the same gradation as the limestone.

Also, substandard and very open-graded aggregates such as sand and poorly graded stream sands were tested. There is a distinct advantage in the use of this type of material in that mixes of them have poor internal friction. They owe what strength can be developed with them to adhesion provided by the binder. These aggregates are sensitive to the strength of the binder; hence, they give a good indication of the strength of the *binder* only. Several of the SULPHLEX formulations made very strong water-resistant mixes with all of the aggregates. Figure 10 indicates how some stress-strain curves on unconfined SULPHLEX specimens compare with curves from asphalt mixes. It will be noted from Figure 10 that the SULPHLEX mixes with limestone provided almost twice the strength that AC-20 showed. Using stream sand as the aggregate, the No. 233 formulation of SULPHLEX gave strengths four times higher. The same increase applied to blow sand; while

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*Dale, John M., and Allen C. Ludwig, Advanced Studies of Sulfur-Aggregate mixtures as Structural Materials, Technical Report No. AFWL-TR-68-21, Air Force Weapons Laboratory, Kirtland AFB, N.M., Oct. 1968.

TABLE 4. COMPOSITION AND SUMMARY OF PHYSICAL TEST RESULTS ON SULPHLEX MIXES

(English System)

Composition			No. 230			No. 126			No. 233			No. 433			AC-20	
Sulfur			70%			61%			70%			70%			—	
Dicyclopentadiene			15			13			12			13			—	
Dipentene			15			—			10			7			—	
Vinyl toluene			—			13			8			—			—	
Coal Tar			—			13			—			—			—	
Tall Oil Pitch			—			—			—			10			—	
AC-20			—			—			—			—			100%	
PHYSICAL TEST	°F	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1 wk	6 mo	1 da	1wk	6 mo
Tensile Strength, ASTM	-20	470	570	600	714	714	750	1285	1642	1700	1142	1570	1700	400	400	400
(C496) in psi	77	285	528	600	428	571	714	442	500	542	428	428	400	228	228	257
	140	100	114	100	70	70	85	42	57	57	42	42	42	42	42	42
Compressive Strength,	-20	3628	4414	4571	—	—	—	2400	2600	2857	3857	4285	5000	4000	4000	4000
ASTM (C39) in psi	77	1814	1857	2000	—	—	—	2400	2400	2430	2430	2714	2800	1285	1300	1300
	140	500	685	714	—	—	—	314	357	370	257	257	271	257	271	271
Typical Sp Gravity (D71)	77		2.36			2.39			2.40			2.40			2.31	
Max Flexural Strength	77		570			540			too flexible			too flexible			too flexible	
ASTM (C78) in psi																
Marshall Stability	140	1200	4700	6600	1300	2200	5500	1100	1870	2860	1100	2000	3100	440	1550	1760
Marshall Flow	140	15	16	17	9	15	22	15	17	17	9	10	12	12	14	15
ASTM (D1559) in lbs																
Abrasion Resistance	77	1/8"				1/8"			1/8"			1/8"			1/8"	
2000 Rev of Carbo																
Stone																
Thermal Shock, 77° to	-20		no effect			no effect			no effect			no effect			no effect	
Freeze-Thaw, cycles																
140 to	-20											—				
San Antonio Limestone			100			120			117			—			120	
Basalt from Roseburg, Ore.			57			65			20			—			71	
Riv. grav. from Holbrook, Ar.			45			50			57			—			60	
Wet-Dry Comp Ratio																
ASTM (D1075) 6% Binder	77		0.8			0.8			0.8			0.7			0.9	
Mod of Resilience,	74		2.2 x 10^6			3.4 x 10^6			3.3 x 10^6			—			.94 x 10^6	
Schmidt in psi																

1 psi =6,894 pascals, 1 lb =.454 kg, 1 Btu/in/h/ft^2 °F =6.94 W/m/K/ and °C =(°F-32)/1.8

with crushed granite, the strength shown by the AC-20 mix was as high or slightly higher than that shown by the SULPHLEX mix. Marshall test data confirm these tendencies. Apparently, for aggregates, where cohesion is definitely necessary to provide good stability (such as rounded, fine grain materials), SULPHLEX provides that cohesion in large amounts. On the other hand, where stability is largely a function of the large angular particles (such as for crushed granite), there is little need for the cohesion provided by SULPHLEX. Mixes of sulfur materials and calcareous aggregates are examples of a special case where strong bonds are inherent.

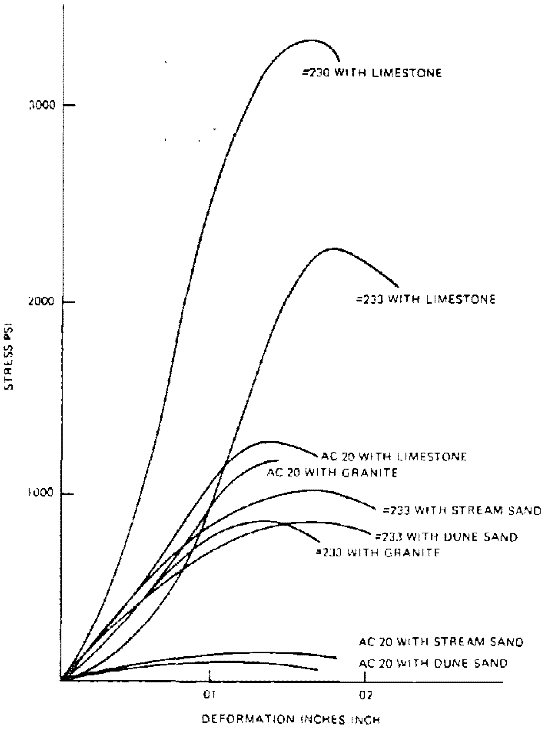

Figure 10. Stress-deformation curves resulting from the use of various SULPHLEX binders and asphalt with the same well graded aggregates (6% wt binder).

ECONOMICS

At the initiation of this program, the principal emphasis was on the technical feasibility of modifying elemental sulfur into an asphalt-like product. However, it was realized that if the resultant products were cost competitive with asphalt at today's prices, its potential for early implementation would be enhanced.

As discussed earlier, the rationale at the initiation of the program was to screen a large number of low-cost additives first. If this was unsuccessful, then more expensive additives would be screened, and as a last resort, laboratory manufacture of modifiers would have been attempted. The arbitrary decision was made to first screen materials with a cost of 40 cents per pound or less. From past experience it was known that numerous potential materials fell within this cost restriction, and indeed, a number of potential materials were found. There were exceptions to this cost restriction as materials on hand in the laboratory were also screened.

The prices for a selected number of modifiers are shown in Table 5. Styrene is not a preferred modifier but it is chemically similar to vinyl toluene. It is interesting to observe the price change for both since January 1977. The price quoted for the coal tar is for a roofing grade tar. Prices were not quoted for ungraded tars, although prices of $100 per ton were quoted by manufacturers during the course of the project. The sulfur prices are the quoted Gulf Coast price, except in the last column, the $53/l ton quote is for Chicago. Sulfur prices are quite variable, depending on the source; and even though the quoted price was $61/l ton in December 1978, sulfur was purchased for the project at $45/ton for solid sulfur, and $52.50/l ton for molten sulfur. In addition, Canadian sulfur continues to be quoted at $25/l ton, f.o.b. Canada.

Thus, the economics for only the materials can vary depending on the sources of materials selected, as well as the area of the country. If the prices are selected directly from Table 5 and the cost of several formulations are calculated as in Table 6, it can be seen that the prices have increased for SULPHLEX since the initiation of the laboratory portion of this project. In general, the prices for most of the formulations are within the cost range of current asphalt prices. These prices can be improved upon if, for example, several things are taken into consideration.

TABLE 5. QUOTED CHEMICAL PRICES
(Car load lots)

Chemical	Quoted Price* per lb			
	Jan. '77	July '77	Dec. '78	Sept. '79
Styrene	.21	.21	.185	.35
Vinyl Toluene	.325	.325	.365	.445
Dicyclopentadiene	.112	.112	.112	.155
** CDC (impure DCPD)	--	.05	--	.08
Dipentene	.08	.08	.08	.08
** Tall Oil Pitch	.05	--	--	.05
1,5 cyclopentadiene	.70	.70	.70	.70
Coal tar (roofing grade)	$128/ton	$128/ton	$128/ton	$128/ton
Sulfur	$60/l ton	$60/l ton	$61/l ton	$53-71/l ton

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* Chemical Marketing Reporter

** From manufacturers' price sheets

Metric Equivalents
1 pound = .454 kg
1 ton (short) = 907 kg
1 ton (long) = 1020 kg

TABLE 6. CALCULATED SULPHLEX COSTS BASED ON QUOTED PRICES

		No. 233				No. 126				No. 230	
	%Wt	Jan. '77	Sept. '79		%Wt	Jan. '77	Sept. '79		%Wt	Jan. '77	Sept. '79
S	70	$1.89	$2.22	S	61	$1.65	$1.93	S	70	$1.89	$2.22
VT	8	2.60	3.56	VT	13	4.23	5.79	CDC	15	.98	1.58
CDC	12	.78	1.26	DP	13	1.04	1.04	DP	15	1.20	1.20
DP	10	.80	.80	CT	13	.83	.83				
		$6.07/100 lb	$7.84/100 lb			$7.75/100 lb	$9.59/100 lb			$4.07/100 lb	$5.00/100 lb
		$121.40/ton	$156.80/ton			$155.04/ton	$191.84/ton			$81.40/ton	$100.00/ton

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Metric Equivalents
1 pound = .454 kg
1 ton (short) = 907 kg
1 ton (long) = 102 kg

S—Sulfur
VT—Vinyl toulene
CDC—Impure dicyclopentadiene
DP—Dipentene
CT—Coal tar

As already discussed, the sulfur price will fluctuate, depending on location and source. Secondly, the quoted prices are not contract prices. For example, several manufacturers have indicated that large quantities in bulk, on long term contract would be substantially different from a small quantity, one time purchase. This is pointed out in Table 7 where the actual and projected costs for the three formulations used in the experimental road construction in December 1978 are shown. The costs reflected in the Actual Cost column were calculated to be what the cost per ton for the formulation actually was based on what the chemical ingredients cost the project. While the sulfur was lower than the quoted price, the modifiers were considerably higher because they were purchased in drums, and in several instances from distributors, because the manufacturer did not package in drum quantities. As a result, the actual costs were approximately twice the projected cost. The Projected Cost column, reflects what the costs might be, based on large quantity purchase at the job site.

TABLE 7. ACTUAL AND PROJECTED COSTS OF SULPHLEX FORMULATIONS FOR EXPERIMENTAL ROADWAY DECEMBER 1978

Formulation	Actual Cost $/ton	Projected Cost $/ton
No. 233	$237.00	$112.00
No. 126	240.00	128.00
No. 230	131.00	73.00

Because the modifier prices ultimately determine the SULPHLEX cost, it is desirable to produce functional formulations from the lower cost materials. Formulation No. 433 is an example.

TABLE 8. PROJECTED CURRENT COST FOR FORMULATION No. 433

	Composition No. 433	Unit Cost	Component Cost
Sulfur	70 lb	$45/1 ton	$1.40
CDC	13 lb	8¢/lb	1.04
Dipentene	7 lb	8¢/lb	.56
Tall Oil Pitch	10 lb	5¢/lb	.50
			$3.50/100 lbs or $70.00/ton

The costs discussed are only materials costs and do not reflect manufacturing or processing costs. Because the processing is relatively simple, it is expected that the manufacturing costs will ultimately be relatively low, such that bulk SULPHLEX prices should be in the range of today's asphalt prices.

What the ultimate SULPHLEX prices will be as sulfur and chemicals are produced from coal and coal by-products may not be as important as the fact that availability should be assured in a world where petroleum is becoming scarcer, and consequently, more expensive.

SUMMARY OF RESULTS

This program has established that it is technically and economically feasible to produce an asphalt-like material from sulfur, using hydrocarbon modifiers that can be obtained from nonpetroleum sources. SULPHLEX, the name given to these highly modified sulfur formulations, is a family of materials that, when used as binders with aggregate, have the potential of producing flexible concretes with properties like those of asphaltic concretes or rigid concretes with properties similar to Portland cement concretes, or concretes with properties intermediate between these extremes.

In physical properties, the SULPHLEX binders compare favorably with an AC-20 grade asphalt. A hardening effect has been observed in the SULPHLEX binders such that penetration values do change with time. The flash point for the SULPHLEX binders is in the range of 350-370° F (176-188° C), somewhat lower than for an AC-20 asphalt.

The mechanical properties of the concretes using SULPHLEX as the binder compare favorably with asphalt or Portland cement concretes. SULPHLEX as the binder for the limestone aggregate used from the San Antonio area gives better Marshall stability and unconfined compressed strengths than did asphalt as the binder. For other aggregates investigated, there were no significant differences in these properties. Resistance to freeze-thaw cycling was good, although the wet/dry stability ratios are less than for asphaltic concretes.

A 620 ft experimental roadway was built in December 1978 using three different SULPHLEX formulations. It was demonstrated that SULPHLEX could be prepared in large quantities and substituted directly for asphalt. No changes or modifications were made in the batch plant or in the application equipment normally used for asphaltic concretes. The performance of this experimental roadway has been excellent and evaluations will continue. Additionally, preliminary evaluations indicate that there is the potential for SULPHLEX emulsions, SULPHLEX rejuvenators for asphaltic concretes, and SULPHLEX seal coats and joint sealants.

The manufacture of SULPHLEX in the laboratory and in scaled-up field units has been reasonably simple. Figure 11 is a chart showing how SULPHLEX might be integrated into the refining industry.

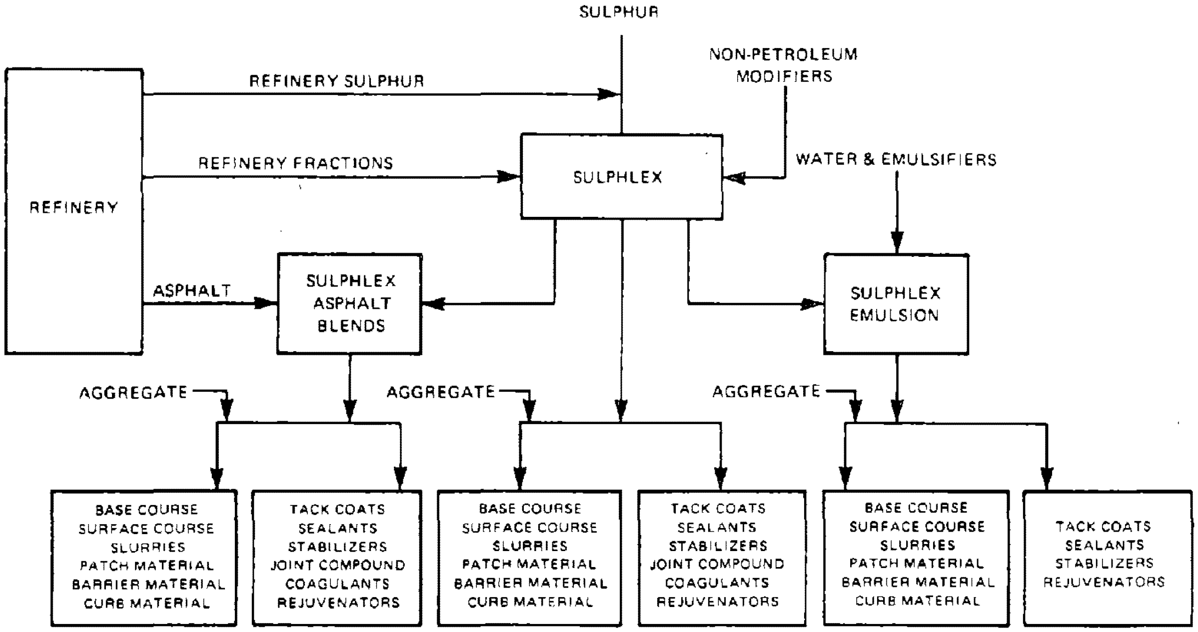


Figure 11. Integration of SULPHLEX into the refining industry.

RECOMMENDATIONS FOR FUTURE RESEARCH

This program has demonstrated that sulfur can indeed be altered so that the resultant SULPHLEX binders can be used to produce pavements that have properties like asphaltic concrete, Portland cement concrete, or a new family of concretes that lie between these two.

Future research must necessarily follow two distinct routes. One is the further development and understanding of the first generation of materials. This includes chemical characterization, production/process research, mix design, pavement design, and ultimately, construction for field evaluation and performance verification. This research effort should be directed to the more promising materials, as developed to date.

The second route for research to follow is the development of the second generation of SULPHLEX formulations. This research should concentrate on improving properties of the first generation materials, as well as investigating new applications.

There are a number of areas that the second generation of materials should improve upon. Formulations No. 230 and No. 233 have an odor which may be objectionable to some. This is believed due to the dipentene or a reaction between the dipentene and sulfur. Formulation No. 453, in which tall oil pitch is substituted for dipentene, has a reduced odor, improved tackiness, and less tendency to harden; it is an example of the direction of second generation work. The development of the second generation materials should also be concerned with improving adhesion to all types of aggregates, particularly the granites.

A concerted effort needs to be directed toward evaluating the modifiers from different sources as well as the effect of reactant purity upon ultimate properties. In conjunction with this, quality control needs to be established in the manufacture and evaluation of the various formulations. It has been observed that some formulations have a tendency to harden with time and the degree of change can vary from batch to batch.

Considerable effort should also be directed to applications besides pavement binders. Principal emphasis on the pavement binders has been to use low-cost modifiers so that the resultant costs are competitive with current asphalt prices. Some potential applications where costs may not be as critical are joint sealants, rejuvenators, seal coats, and bridge deck formulations. A whole family of materials could be developed for these applications.

APPENDIX A
REPORT
ON
THE FIRST AGGREGATE MIX AND LAYDOWN
OF
SULPHLEX WITH COMMERCIAL EQUIPMENT

Under Federal Highway Administration Contract DOT-FH-11-9111, work began early in 1976 to develop materials and techniques for improving the engineering properties of sulfur for use on roadways. By August of 1978, a number of sulfur formulations for the preparation of both the flexible and rigid type of roadway surface had been developed, and the Federal Highway Administration issued Modification No. 942-41-23-13-8192-34G1-8-2582 to the original contract calling for the placement of test sections within the Southwest Research Institute (SwRI) facility.

As a prelude to construction of these test sites, a trial run at a commercial plant using a SULPHLEX mix was deemed necessary to determine the heating and binding characteristics of the material in a large-scale operation. Arrangements were made with Mr. Tom Warren, head of the Warren Equipment Company, Contractor, to prepare the foundation for the trial run and haul the SULPHLEX No. 230 binder from SwRI to the batch plant 18 miles (29 Km) north of the trial site.

At the batch plant, 7% SULPHLEX binder was mixed with the Standard Grading D Texas Highway Department surfacing and discharged into a truck. The truck hauled the mix back to a 30 ft x 35 ft (9.1 m x 10.7 m) site just west of the SwRI Sulfur Lab and unloaded it on the ground. A front end loader transferred the mix from the pile to the Power Box laydown machine which placed the mix approximately 3 in. (7.6 cm) deep on a very wet subgrade previously compacted to 95% AASHTO T-99 value by a Dyna Pac roller. The subgrade was in good condition a month later when the roadway sections were placed, even though the weather was cold and wet.

Plans for the Roadway

The Warren Equipment Company of San Antonio was selected to do the construction work. This included preparation of the base, hauling the binder 18 miles (29 Km) to the batch plant, and laying the mix after it had been received from the batch plant.

Mr. David Eldridge and Mr. Roger Hopper of McDonough Brothers, Inc. agreed to store and reheat the binder, mix it with the Standard Texas Highway Department specification crushed limestone, and send it by dump truck to the test site. Their plant was a modified stationary Cedar Rapids, capable of 35 second mixing of 6000 lb (2724 Kg) batches. The binder temperature was kept near 300° F (149° C) and the aggregate temperature was near 320° F (160° C). These temperatures resulted in a temperature of approximately 280° F (138° C) in the mix inside the truck bed when delivered. The gradation of the crushed limestone aggregate was as follows:

% Passing 1/2 in. =100%
% Passing #4 =50%
% Passing #200 =7%.

The roadway sections were planned to test three different SULPHLEX formulations on a strip of roadway 620 ft (189 m) long and 24 ft (7.3 m) wide. Formulation No. 233 was similar in properties to an AC-10 cement and considered to be essentially a flexible binder. It was planned for placement in two 1-1/2 in. (3.8 cm) lifts for a 3 in. (7.6 cm) layer at 6% binder and 8% binder levels.

Formulation No. 230 continues to develop strength and rigidity for about 28 days and is analogous in many respects to Portland cement. It was planned for trial at 6% binder level in an 8 in. (20.3 cm) lift and at 8% binder level in a 3 in. (7.6 cm) lift.

Formulation No. 126 has properties which fall about halfway between the other two. It was planned for trial at 8% binder level in an 8 in. (20.3 cm) lift and at 6% binder level in a 3 in. (7.6 cm) lift.

In addition to these six trial sections with SULPHLEX binders, a 3 in. (7.6 cm) thick section of Standard Texas Highway Department asphalt mix and an 8 in. (20.3 cm) thick section of Standard Texas Highway Department Portland cement concrete were planned for control and comparison.

Preparation of the Roadbed

The three months preceding the December trial date had been wet and relatively cold with a minimum temperature of 14° F (-10° C). Characteristics of the subgrade material at the construction site were as follows:

Slope - 0% to 1%. Drainage-poor. No fill.
Gradation - 90% passing #4, 80% passing #10, 70% passing #200.
Max. dry density - 106 pcf (1700 Kg/m^3) at 20% moist (also average field moisture).
Field CBR - AVG =8 at 20% moist (10% calcareous stones).
Cover required - Approximately 7 in. (18 cm) for 700 vpd and 10% trucks (assuming 3 in. (7.6 cm) of asphalt mix surfacing).
Atterburg Limits - LL=51, PL=37, PI=14 (Calcareous).

Characteristics of the Standard Texas Highway Department Item 242 Type A crushed limestone base placed 4 in. (10.2 cm) thick were as follows:

Atterburg Limits - LL-21, PL=17, PI=4.
Field CBR - 83 at 5% moisture and 138 pcf (2210 Kg/m^3).
Gradation - 100% passing 2 in. (5.1 cm), 29% passing #4, 10% passing #200.

Preparation of the Binder

The SULPHLEX binders were prepared in steel bins 4 ft x 4 ft x 8 ft (1.2 m x 1.2 m x 2.4 m) heated on four sides and the bottom by oil at approximately 300° F (149° C). The bins were covered by 3/4 in. (1.9 cm) plywood tops.

The bins were charged as follows:

	Formulation No. 230	**Formulation No. 126**	**Formulation No. 233**
Starting Date	**Dec. 11, 1978**	**Dec. 15, 1978**	**Dec. 15, 1978**
Date of Transfer to Batch Plant	Dec. 16, 1978	Dec. 18, 1978	Dec. 19, 1978
% Commercial Sulfur	69	60	69
% Commercial grade DCPD	11.25	9.75	9
% Pure DCPD	3.75	3.25	3
% Commercial grade Dipentene	15	---	10
% Vinyl Toluene	---	13	8
% Coal Tar	---	13	---
% Polysulfide Catalyst	1	1	1
Max Temp° F	300° F (149° C)	310° F (154° C)	310° F (154° C)

Approximately 7500 lb (3400 Kg) of binder was made in each bin, and it took two bins to make enough of each formulation for the planned test sections. The losses in making, transferring, and mixing the binder with aggregate for this experimental work are estimated to be as follows for each formulation (2 bins):

Left in bins (2 bins) (unable to pump out)	700 lb (318 Kg) =6%
Evaporation of modifiers from tanks and bins	100 lb (45.4 Kg) =1%
Left in transfer tanks (mobile tanks and pumps)	200 lb (45.4 Kg) =1%
Left at batch plant (unable to pump out)	2000 lb (908 Kg) =16%

Loss out of 12,000 lb (15,448 Kg) total =2900 lb (1317 Kg) =24%

Construction of the Experimental Sites

Because each SULPHLEX formulation had been planned to have at least two test sections (6% and 8%), and each section would have at least 2 lifts (3 for the deep strength sections), it was realized that considerable time would be necessary to place all of the material mixed at the batch plant for each formulation. Consequently, a slight modification was made in the initial layout of the test sections. Also, plans were made to dump certain truck loads on nearby roadways and hold others under a demurrage agreement. The Barber Greene asphalt paver was loaded by means of a front end loader. No trucks dumped directly into the Barber Greene. This procedure resulted in some loss of temperature and uniformity of mix, but it was found to be necessary in view of the short length of the test sections and the way that they were interspersed.

A sketch of the test sections is shown later in Table 11 including the temperature history, times of laydown, and rolling. Table 11 also lists the time schedule of the work performed in placing the sections, except for the concrete test section which was placed on December 7, 1978, at temperatures between 35 and 45° F (1.7-7.2° C). The humidity was approximately 90%, and a slow drizzle was in progress at the time when the broom finish was applied (10:00 p.m.). The surface was covered with straw and a polyethylene sheet the next morning and allowed to cure for one week. The temperature during the week ranged from 15 to 55° F (-10 to 13° C). At the end of the week, the polyethylene sheet and the straw were removed and weakened-plane joints were sawed 1-1/4 in. (3.2 cm) deep down the centerline and transversely at 13 ft (4 m) spacings.

Test on Materials

Samples of the binder and the mix were taken before laydown. Tests performed on the binder alone are shown in Figure 12. The viscosity was determined by means of the Shell Cup No. 4. All of the binders met the 100 cm + criteria for ductility.

Physical tests on the aggregate mix are shown in Table 9. The *cores* were taken with a 3-3/4 in. (9.5 cm) diameter diamond ring core bit 30 days after laydown. The density was determined by immersion in water, ASTM D2726. There was considerable variation in the density (and consequently the percent voids) in the cores from the different sections, tending to verify observations during construction that compaction was not uniform due to differences in temperature of the mixes at laydown. Sections No. 9 and No. 10 were examples of extremes, where the mix was placed and rolled at 100° F (38° C). These were very short sections primarily placed to determine whether SULPHLEX would compact at very low temperatures.

Marshall Tests were performed on specimens compacted in the lab on reheated mixes. Material with 6% binder tended to have a lower density than mixes with 8% binder. This was also true for the cores, and this variation in density of the cores may depend on the inherent ability of the particular mix to compact well. The Marshall Test results also showed considerable variation, wherein strength varied *inversely* with binder content except for formulation No. 230, which is the most rigid of the three formulations used. It does appear that for *flexible* formulations of SULPHLEX, 8% binder is too high, at least as indicated by the Marshall Stability Test. Actually, values such as 7000 lb (31.1 KN) for the Marshall Stability Test indicate that the mix has cemented up into a rigid condition not affected very much by temperatures up to 140° F (60° C). Marshall flow values showed very little variation on this reheated material.

Resilient Modulus values on this reheated material were determined by the FHWA Materials Division.

The Deflection was measured with the Benkelman Beam using an 8000 lb (3632 Kg) dual tire wheel load in the outside wheel paths. Values determined using the inside wheel paths were about 20% lower. Deflection, as well as skid resistance, was also measured by the Texas State Department of Highways and Public Transportation. These measurements are reported in Tables 9 and 10. As expected, the deflection values for the deep strength sections were low, and the values for the 3 in. (7.6 cm) thick section were below the 0.040 in. (0.1 cm) values usually considered to be the dividing point between acceptable and marginal durability.

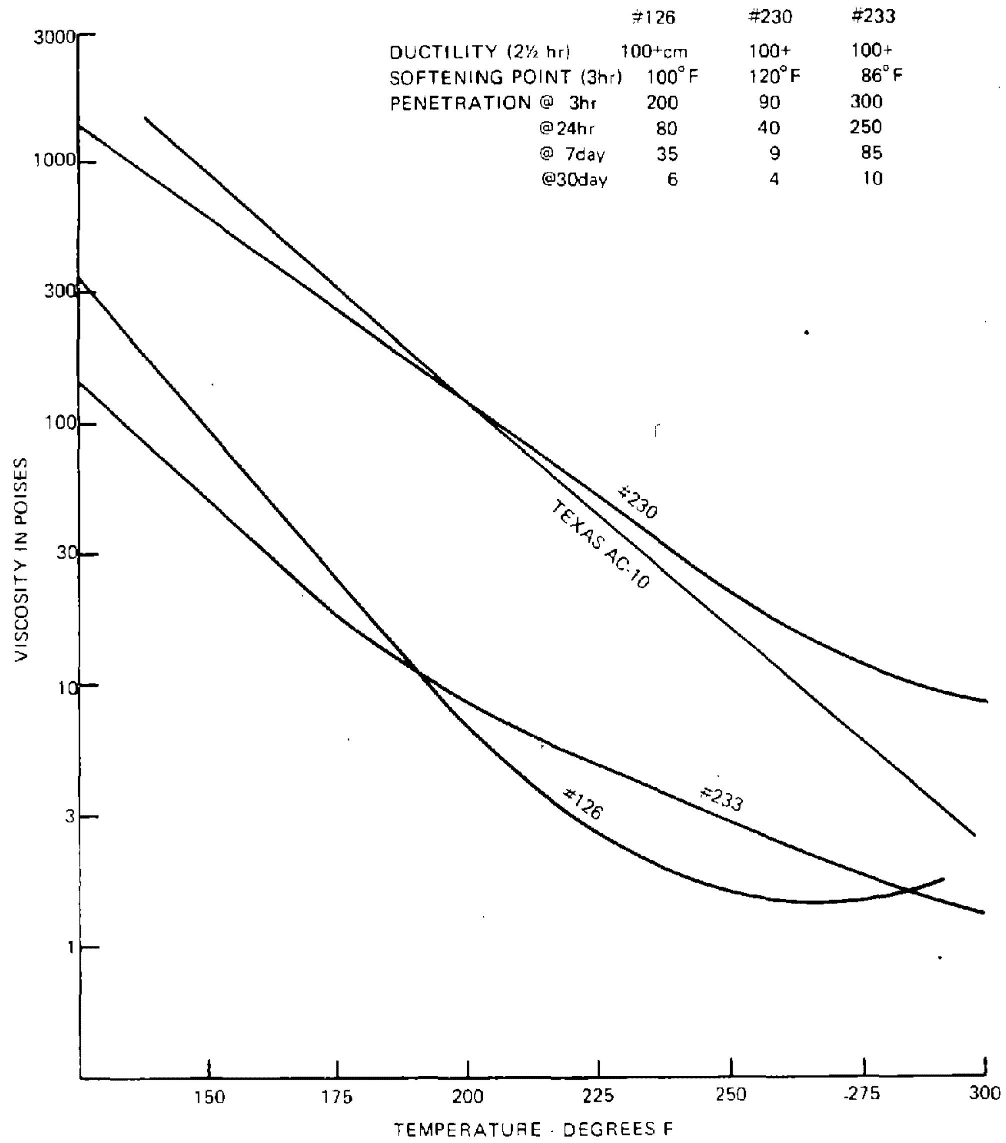
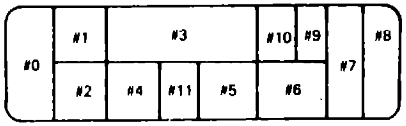


Figure 12. Viscosity-temperature curves for binders used in experimental roadway.

TABLE 9. PAVEMENT PROPERTIES MAY 1979

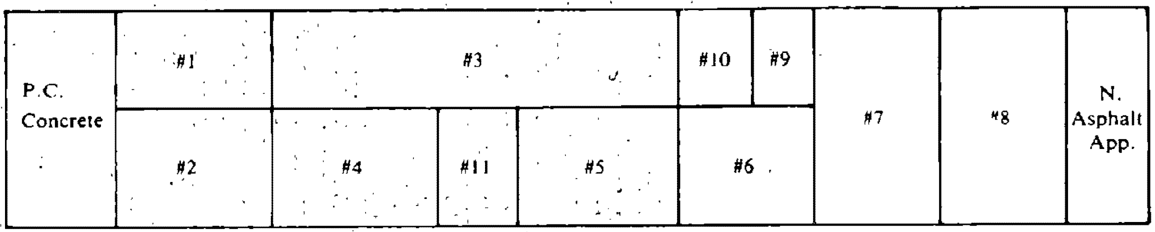
SwRI SULPHLEX TEST SECTIONS



CONDITION IN MAY 1979

NUMBER THICKNESS	CONDITION IN MAY 1979	AVERAGE POUNDS/FT³ FOUND IN CORES	POUNDS/FT³ FOUND BY MARSHALL TEST	% VOIDS IN CORES	% VOIDS IN MARSHALL TEST	AVERAGE MARSHALL LOAD-LBS	MARSHALL FLOW VALUE	MOD. OF RESILIENCE MILLION PSI	DEFLECTION IN INCHES (TEXAS DYNAFLECT)	SKID NUMBER (TEXAS HWY DEPT)	SMOOTHNESS INCHES PER MILE	TEXTURE DEPTH BY SAND PATCH METHOD	28 DAY PSI IN COMPRESSION	28 DAY PSI IN FLEXURE
0-8″	GOOD 5-1/2 SACK/YD³ PC CONCRETE	150		3.0					.003		28.6	.0236	6400	717
1-7″	GOOD #126 BLACK SULPHLEX 8%	147	149	5.0	4.0	1500	11	3.2	.010		16.6	.0169	1280	538 +
2-6″	GOOD 6% BROWN SULPHLEX #230 EXCEPT FOR RAVELING AT COLD CENTERLINE JOINT	140	140	9.0	10.0	2500	11	2.9	.010		20.0	.0318	800	350 +
3-3″	GOOD 4.5% AC-10 ASPHALT MIX	142	143	8.5	8.0	1000	10	0.9	.028	43	3.3	.0122		
4-3″	GOOD 8% #233 BLACK SULPHLEX	147	147	5.0	5.5	1600	10	3.2	.028		3.3	.0138		
5-3″	GOOD 6% #233 BROWN SULPHLEX EXCEPT FOR 12′ OF LONGITUDINAL CRACKING ON SHOULDER	142	142	8.5	8.5	1100	10	2.3	.032	50	2.5	.0249		
6-3″	GOOD 8% #126 BLACK SULPHLEX	144	149	8.0	4.0	1400	11	3.2	.032	59	3.5	.0257		
7-3″	FAIR 6% #126 BLACK SULPHLEX DUE TO FOUR BAD POT HOLES IN SOUTH END TRANSITION ZONE	142	136	8.5	13.0	1200	9	0.9	.030	54	5.0	.0257		
8-3″	FAIR 8% #230 BROWN SULPHLEX DUE TO RAVELING ON EAST HALF	134	144	17.5	7.0	1800	11	2.6	.035	50	7.9	.0249		
9-3″	POOR 6% #230 BROWN SULPHLEX DUE TO RAVELING OF MATERIAL PLACED WHEN COLD	–	140		10.0	2500	11	1.8	.039		84.0	.0339		
10-3″	POOR 8% #230 BROWN SULPHLEX DUE TO RAVELING AND POT HOLES FROM COLD COMPACTION	–	144		7.0	1800	9	2.6	.040		298.0	.0339		
11-3″	GOOD 6% #233 BLACK SULPHLEX EXCEPT FOR 13′ OF LONGITUDINAL CRACKING	–	142		8.5	1100	10	2 3	.030	50	3 3	.0169		
12-3″	NORTH END ASPHALT APPROACH POOR	–	–	–	–	–	–	–	.035	–	4.0	–		

TABLE 10
SUMMATION OF AVERAGE OF DEFLECTION AND SKID NUMBER MEASUREMENTS
on the
SULPHLEX ROAD TEST SECTION
December 1979



SECTION LOCATION	Benkleman Deflection	Data Provided by Texas Hwy Dept. Dynaflect Deflection	Surface Curvature Index***	Stiffness Coefficient	Skid Trailer SN	Core Length	Core Density	% air voids
Concrete-BWP*	.003	.003	.020	1.47	-	-	-	-
#1, 8% #126 BWP	.014	.012	.21	.92	-	5.5"	146 pcf	5 1/2
#1, 8% #126 RWP**	.027	-	-	-	-	-	-	-
#2, 6% #230 BWP	.015	.009	.135	1.0	-	6.7"	138 pcf	11
#2, 6% #230 RWP	.021	-	-	-	-	-	-	-
#3, Asphalt BWP	.048	.023	.97	.60	-	3.3"	143 pcf	7
#3, Asphalt RWP	.045	-	-	-	38	-	-	-
#4, 8% #233 BWP	.047	.026	1.24	.47	-	3.7"	146 pcf	5 1/2
#4, 8% #233 RWP	.070	-	-	-	39	-	-	-
#5, 6% #233 BWP	.047	.030	1.14	.67	-	2.7"	140 pcf	10
#5, 6% #233 RWP	.092	-	-	-	38	-	-	-
#6, 8% #126 BWP	.045	.036	1.15	.81	-	2.45"	144.5 pcf	7
#6, 8% #126 RWP	.045	-	-	-	50	-	-	-
#7, 6% #126 BWP	.033	.024	.88	.75	-	2.95"	139 pcf	11
#7, 6% #126 RWP	.035	-	-	-	47	-	-	-
#8, 8% #230 BWP	.062	.031	1.07	.75	-	2.75"	136 pcf	13
#8, 8% #230 RWP	.115	-	-	-	41	-	-	-
#9, 6% #230 BWP	.058	.038	1.66	.53	-	.75"	133 pcf	14
#9, 6% #230 RWP	.075	-	-	-	37	-	-	-
#10, 8% #230 BWP	.060	.038	1.45	.67	-	-	-	-
#10, 8% #230 RWP	.075	-	-	-	37	-	-	-
#11, 6% #233 BWP	.030	.033	.90	.94	-	3.0"	144 pcf	7
#11, 6%#233 RWP	.090	-	-	-	41	-	-	-
N. Asp Approach BWP	-	.033	1.08	1.02	-	-	-	-
N. Asp Approach RWP	-	-	-	-	-	-	-	-
Lab Park Lot-West	-	.029	.80	2.23	-	-	-	-
Lab Park Lot-East	-	-	-	-	-	-	-	-

*Between wheel paths

**Right wheel path

***(Def 1 - Def 2)10^2

The Skid Resistance was first measured with the British Portable tester. There has always been some concern that this device does not indicate skid numbers comparable to skid trailers, but the highway departments in California, Colorado and other states have developed correlation charts that can be used with reasonable dependability. In May 1979, personnel from the Texas Highway Department used their skid trailer to measure skid numbers on the sections that could be tested at 40 mph (64 Km/hr) velocity. Certain end sections were too confined to allow vehicle travel at that speed. The test values were in the 50's for both the asphalt and the SULPHLEX sections, indicating reasonably good skid resistance. This data is found in Tables 9 and 10.

The Smoothness Values were obtained by means of a pivot wheel attached to a 24 ft (7.3 m) sled. The graph was analyzed by the California test method 526-C, and provides a relative measure of smoothness between sections. The values of 84 in./mile (133 cm/Km) for section 9, and 298 in./mile (473 cm/Km) for section 10 are indications of the deterioration that took place during the first 6 months of service in cold, wet weather.

Texture Measurements were made using the SAND PATCH procedure. Formulation No. 230, which was mentioned before as being the most rigid, appears to display the greatest depth. It was also one of the most difficult formulations to compact, so the tendency for more voids appears to accompany the tendency for a greater texture depth.

Strength Tests were determined by means of 6 in. (15.2 cm) diameter cylinders and 6 in. x 6 in. x 20 in. (15.2 cm x 15.2 cm x 50.8 cm) beams on the materials used to construct the "deep strength" or "rigid" test sections. The P.C. concrete appears to be exceptionally strong for a 5-1/2 sack/cubic yd mix. The SULPHLEX mixes were compacted in the same way as the Portland cement concrete, that is, by tamping with a 3/4 in. diameter rod. They would have been compacted better and more realistically with a roller. The densities for the SULPHLEX beams and cylinders were approximately 125 pcf (2001 Kg/m3). It was noted that at 7 days, the SULPHLEX mixes flowed when they were loaded. Twenty-eight days after they were made, the loading resulted in a definite break of the specimen instead of a bending or flowing of the mix.

Attempts to Detect H_2S

Through the course of this program, a continual effort has been made to detect any hydrogen sulfide (H_2S) emitted as a by-product from the chemical modification reaction. Hydrogen sulfide at low concentrations has a very distinct and characteristic odor that has never been noted by any laboratory personnel or visitors during operations. There are discernible vapors associated with some of the formulations, particularly No. 230 and to some extent No. 233. Monitoring of these vapors with a MSA hydrogen sulfide detector indicates that they cause discoloration of the tubes in a manner similar to H_2S.

Vapors were collected from the large vats when formulation No. 230 was being prepared. Subsequent tests revealed these vapors to be primarily sulfur with a slightly depressed melting point near 230° F (110° C) as opposed to the normal 248° F (120° C) melting point. Infrared analyses on this material were inconclusive.

On December 13, 1978, after the preparation of formulation No. 233 had been completed, equipment from the SwRI automotive vehicle emissions laboratory was used in an attempt to measure any hydrogen sulfide present above the 7500 lb (3400 Kg) batches. No odor of H_2S was evident. The sample tube was placed 12 in. (30.5 cm) above the molten liquid surface in the vat, and a measured amount of gas sample was absorbed into zinc acetate buffer solutions. The results indicated an H_2S concentration of 1.1 to 1.6 ppm using a spectrophotometer technique relating to the absorbance maxima for a methylene blue-sulfide complex. Although this technique is not a conclusive, qualitative confirmation for sulfide ion alone, it is more discriminating than the MSA detector.

The only instance wherein H_2S was unmistakenly identified was the first delivery of SULPHLEX mixture with No. 233 as the binder on December 19. The SULPHLEX binder was delivered to McDonough Bros.

on Monday evening at 3 p.m. and held in the asphalt vat at 300° F (149° C) overnight. As the trailer truck loaded with mix passed by the construction site, low levels of H_2S were detected. However, as soon as the material was dumped on the ground, no further H_2S was in evidence.

It is thought that the SULPHLEX reacted with some residual asphalt in the vat at 300° F (149° C), because this was the only batch to have been stored at this temperature for any length of time and was the only batch with which H_2S was detectable.

General Observations

The single most important observation made in the construction of the experimental roadway has been that all of the SULPHLEX binders, whether rigid or flexible, handled in a manner identical to asphalt. No modifications to the batch plant, trucks, or pavement laying equipment were necessary. In the laydown, conventional asphalt laying and handling techniques were also used without any changes. This is viewed as a major advantage. The weather conditions were not ideal for laying flexible pavements. The sky was overcast; temperatures varied between 50° and 60° F (10° C and 15.6° C) with the relative humidity being 80-90%. 1978 had been an abnormally wet year and the subgrade was essentially saturated with water. In spite of these difficulties, the experimental roadway appears to be performing exceptionally well. Both sections of the rigid formulation showed some signs of raveling initially but this ceased in a short time. One section of the rigid formulation and one section of asphalt control have failed, but both of these sections were laid at the end of the day when the mix temperatures were at or below 100° F (38° C). The rigid SULPHLEX section has been patched with cold lay asphalt and is still serviceable. Attempts will be made to keep this section in service as long as possible.

Thus far, the SULPHLEX pavements have been performing in a manner similar to the asphaltic pavement. It is virtually impossible to tell the SULPHLEX pavements from the asphaltic pavement on the visual appearance of the sections alone.

From the performance of the three SULPHLEX binders used in the construction of the experimental roadway, the feasibility of producing pavement binders from sulfur has been established. Continued laboratory investigation of additional modifiers should produce a broad base from which to choose, and design studies should produce the optimum materials and techniques required to realize the full potential of SULPHLEX as an alternative to asphalt and Portland cement.

Figure 13 shows the two large open-top vats in which the 51,000 lb (23,154 Kg) of SULPHLEX formulations were prepared. When reacted, each batch was transferred to a conventional asphalt trailer and held until required by the hot mix plant. In Figure 14, a SULPHLEX concrete is being applied using a Barber Greene laydown machine. No problems of any type were encountered and for all practical purposes this was a typical "asphalt" job. Figure 15 is an overall view of the SULPHLEX roadway in June, 1979, six months after installation. Typical traffic conditions are approximately 1000 vehicles per day, with 10% of these being heavy trucks. Although traffic is light, abuse of the roadway has been great. Figure 15 shows the affects from the Institute tandem wheel crane riding the edge of a SULPHLEX test section. Other scars include cleat marks from a tracked front end loader, gouge marks from a back hoe, and various scrapes and gouges from dragging heavy equipment. At the end of one year's exposure, the roadway is holding up exceptionally well compared to the controls. The only sections that have failed have been sections 9 and 10 (see Figure 11) wherein the application temperature for the rigid mix was near 100° F (38° C). In contrast, section No. 6 adjacent to 9 and 10 was the same temperature when applied but its performance is excellent.

Sections 9 and 10 have been patched with cold mix asphalt over the year. The latest repair attempt has been to seal coat with SULPHLEX formulation No. 233 chipped with 1/2 in. (1.3 cm) limestone. Thus far, this has been very successful.

The few failures that have occurred in some sections of the SULPHLEX, as well as asphalt control, are subbase failures, causing the typical distress cracks.

Tables 11 and 12 are the construction logs for December 18 and 19, 1978.

Table 13 is a 1980 update showing a summation of surface characteristics on the SULPHLEX road test sections.

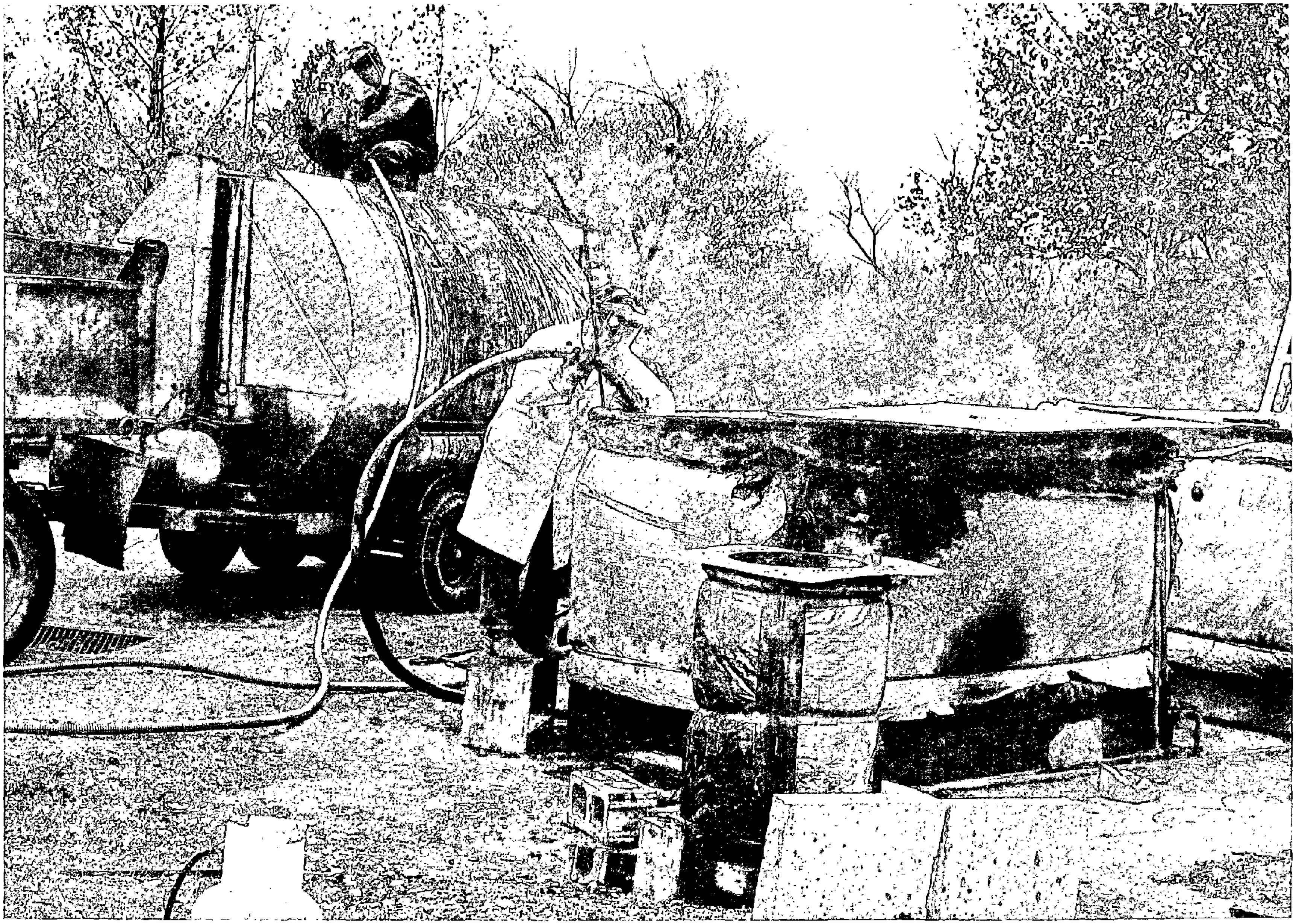


Figure 13. SULPHLEX preparation in open vats.

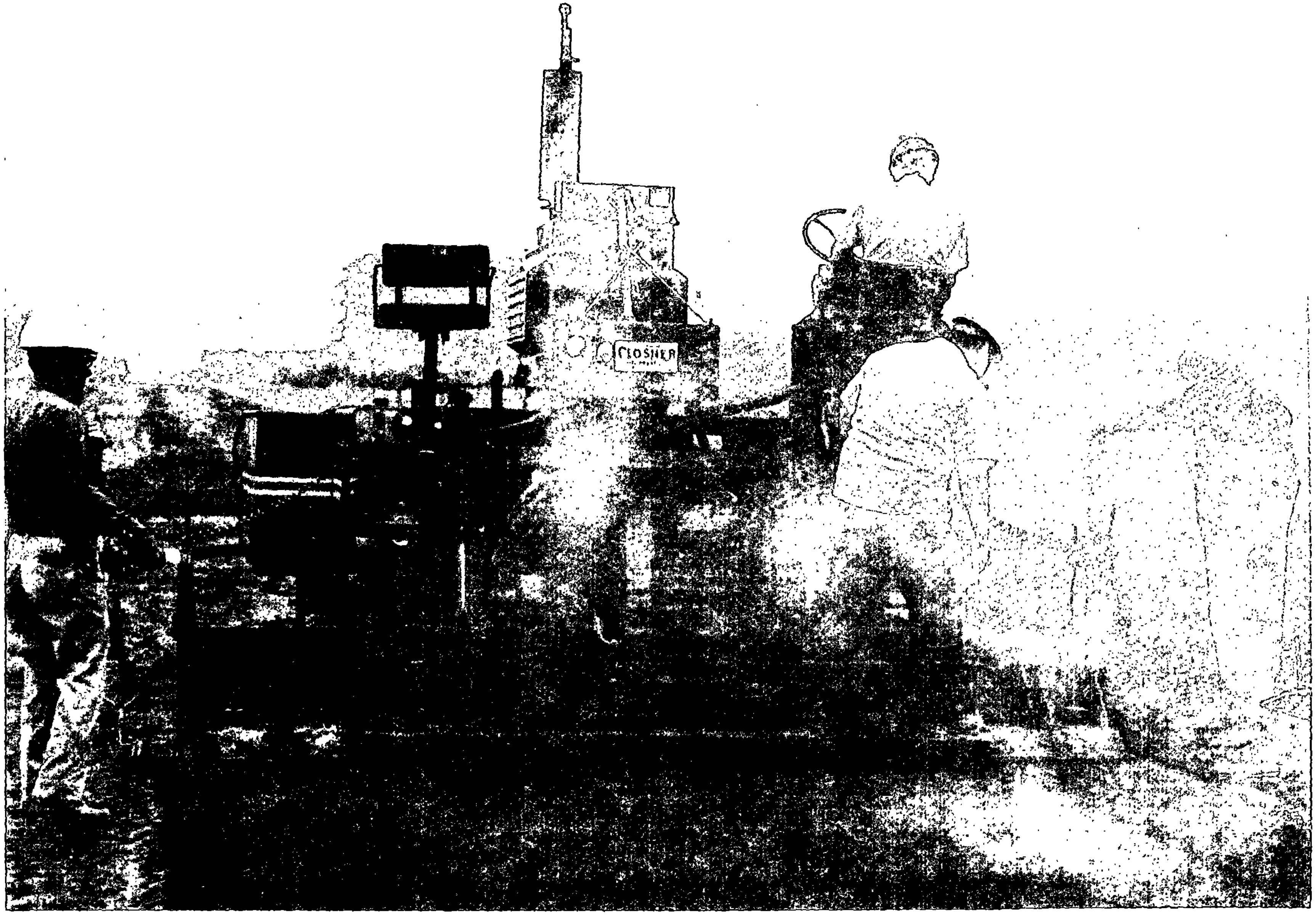


Figure 14. Laying SULPHLEX pavement with conventional equipment.

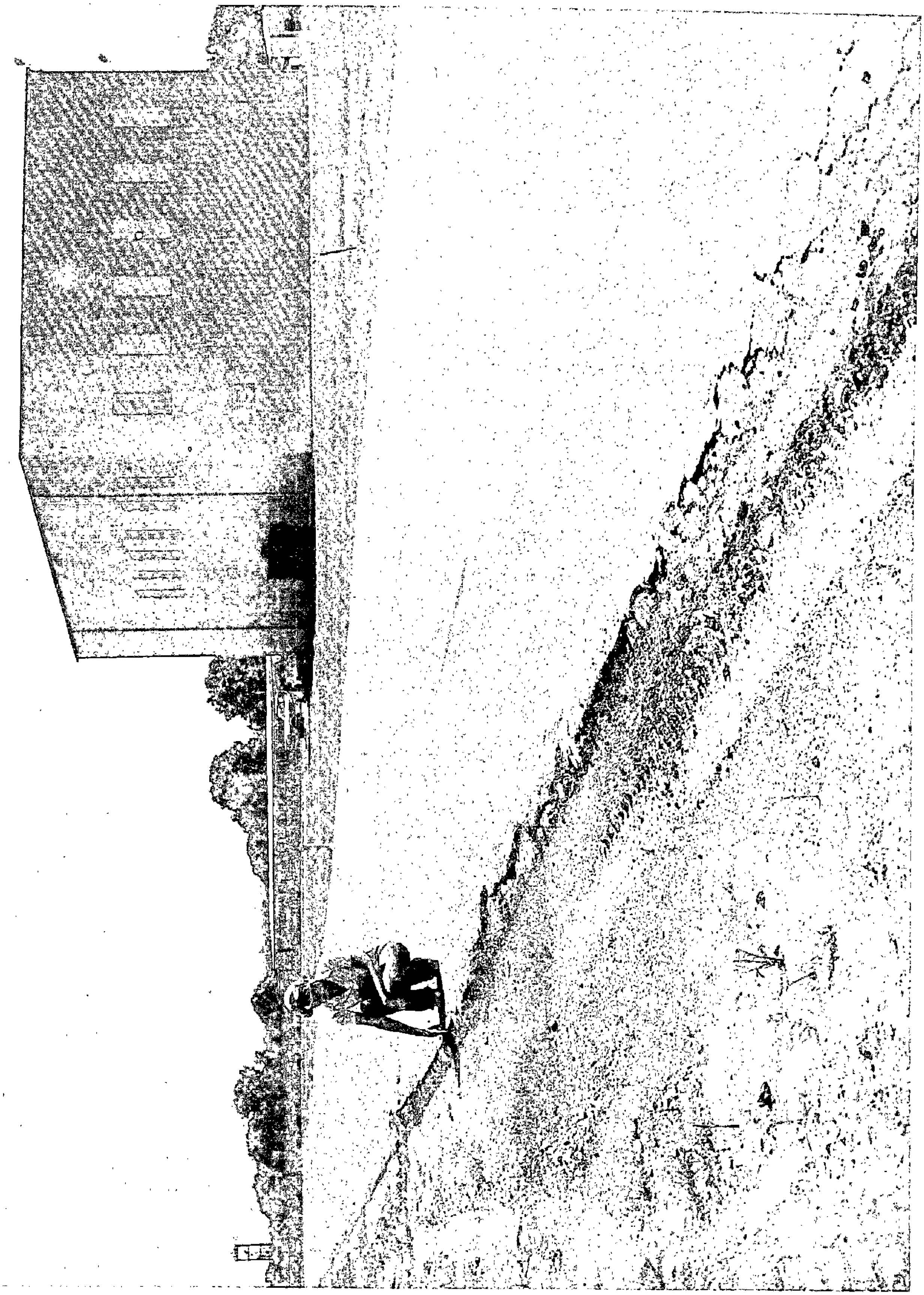
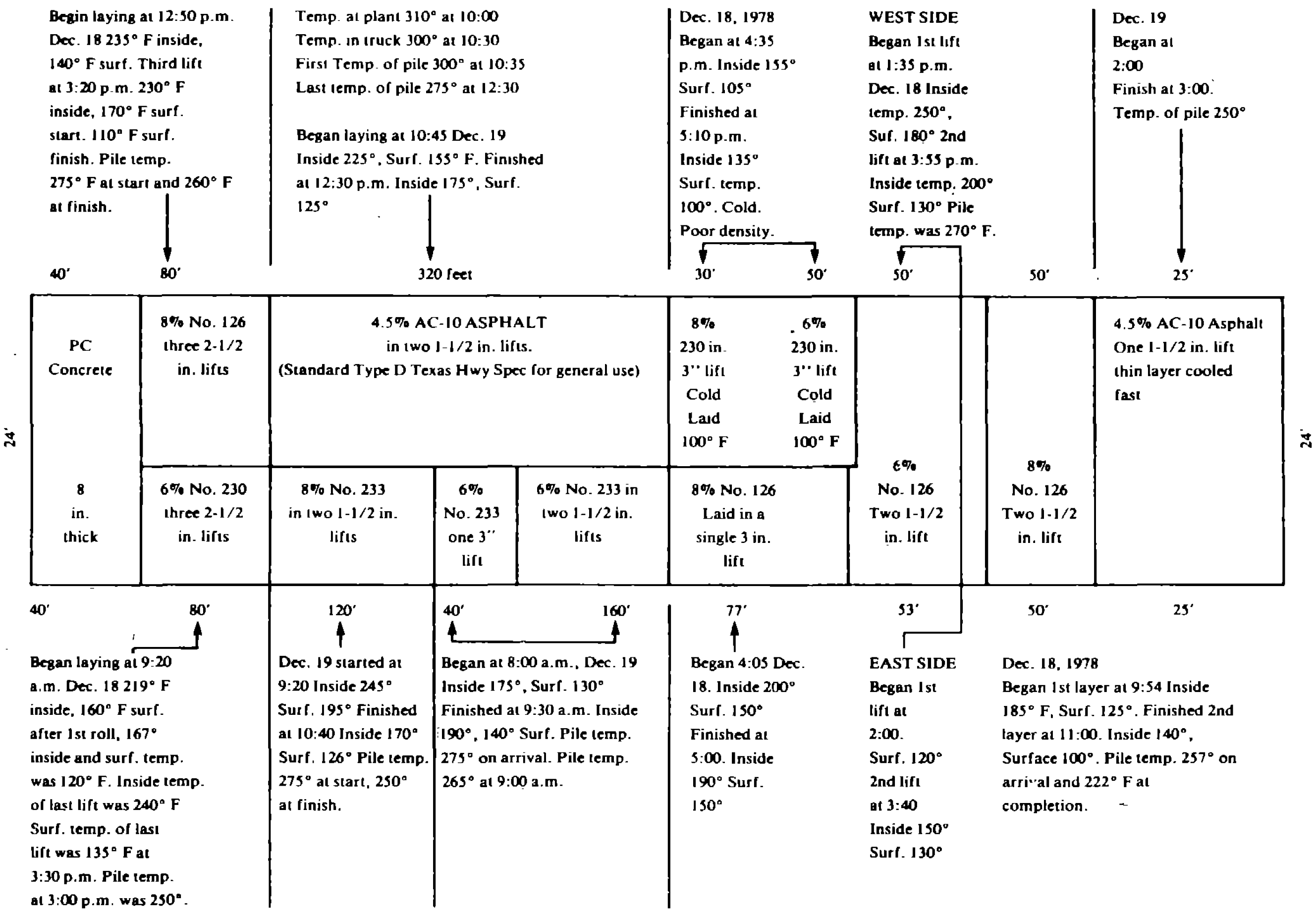


Figure 15. Overall view of SULPHLEX roadway.

TABLE 11. CONSTRUCTION LOG FOR DECEMBER 18, 1978



Begin laying at 12:50 p.m. Dec. 18 235° F inside, 140° F surf. Third lift at 3:20 p.m. 230° F inside, 170° F surf. start. 110° F surf. finish. Pile temp. 275° F at start and 260° F at finish.

Temp. at plant 310° at 10:00
Temp. in truck 300° at 10:30
First Temp. of pile 300° at 10:35
Last temp. of pile 275° at 12:30

Began laying at 10:45 Dec. 19 Inside 225°, Surf. 155° F. Finished at 12:30 p.m. Inside 175°, Surf. 125°

Dec. 18, 1978 Began at 4:35 p.m. Inside 155° Surf. 105° Finished at 5:10 p.m. Inside 135° Surf. temp. 100°. Cold. Poor density.

WEST SIDE Began 1st lift at 1:35 p.m. Dec. 18 Inside temp. 250°, Suf. 180° 2nd lift at 3:55 p.m. Inside temp. 200° Surf. 130° Pile temp. was 270° F.

Dec. 19 Began at 2:00 Finish at 3:00. Temp. of pile 250°

Began laying at 9:20 a.m. Dec. 18 219° F inside, 160° F surf. after 1st roll, 167° inside and surf. temp. was 120° F. Inside temp. of last lift was 240° F Surf. temp. of last lift was 135° F at 3:30 p.m. Pile temp. at 3:00 p.m. was 250°.

Dec. 19 started at 9:20 Inside 245° Surf. 195° Finished at 10:40 Inside 170° Surf. 126° Pile temp. 275° at start, 250° at finish.

Began at 8:00 a.m., Dec. 19 Inside 175°, Surf. 130° Finished at 9:30 a.m. Inside 190°, 140° Surf. Pile temp. 275° on arrival. Pile temp. 265° at 9:00 a.m.

Began 4:05 Dec. 18. Inside 200° Surf. 150° Finished at 5:00. Inside 190° Surf. 150°

EAST SIDE Began 1st lift at 2:00. Surf. 120° 2nd lift at 3:40 Inside 150° Surf. 130°

Dec. 18, 1978 Began 1st layer at 9:54 Inside 185° F, Surf. 125°. Finished 2nd layer at 11:00. Inside 140°, Surface 100°. Pile temp. 257° on arrival and 222° F at completion.

NOTE: Mixes appeared to roll best at a temperature between 215° and 220° F. The usual roll pattern of the 3000# Dead Weight compactor (10,000# compaction) was 2 passes with the roller *not* vibrating (breakdown rolling)followed by 2 to 3 passes about 15 minutes later when it had cooled to about 150° with the vibrator on. The appearance of the 3 section of No. 230 placed in layers 3" thick or less indicates that the material should not be placed and compacted at temperatures below 125° F. Texas Department of Highways and Public Transportation Specifications preclude laying mixes when "the air temperature is below 60° and falling, but it may be applied when the air temp. is above 50° and rising." No restrictions are placed on temperature of the mix at time of rolling, but a hot mix must be placed on the roadway at a temperature between 225° and 350° F, and compacted to a prescribed density (usually 95% of laboratory design density).

TABLE 12. CONSTRUCTION LOG BY SECTIONS

SECTION # 2
FORMULATION NO. 126
BATCH TIME 11:08 a.m. to 11:20 a.m.
BATCH TEMP. 260° F

DATE
PERCENT OF MIXTURE 8%
THICKNESS 8"
NO. OF LIFTS 3

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP °F	NO.OF ROLLER PASSES
11:50 a.m.	#1					
12:00 Noon		293°			–	
12.50 p.m.		293°	1	235°	140°	
1:00		275°				
1:05		1	240°	155°	1	
1:10			1	230°	145°	2 vibrator
1:25			1			3 vibrator
1:30			1		105°	4 vibrator
2:20		266°	1	100°		
2:25			2	200°	150°	
2:30	#2		2			1
2:35			2		120°	2 vibrator
2:50			2	185°	110°	
3:00		260°				
3:12			3			1
3:15			3	230°	175°	2 vibrator

NOTES

1. Temp. of stockpile taken 6" deep into pile.
2. Each pass of roller consists of 2 rolls across surface.
3. .005% H_2S measured in cloud of vapors from stockpile after pile was disturbed by loader.
4. Surface seems to roll better at 215 to 220° F.

SECTION #3
FORMULATION NO. 230
BATCH TIME 7:32 a.m. to 7 45 a.m.
BATCH TEMP. 265° to 270° F

DATE December 18, 1978
PERCENT OF MIXTURE 6%
THICKNESS 8"
NO. OF LIFTS 3

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO. OF ROLLER PASSES
8:00 a.m.	#1	266° to 284°				
9:10		266° to 284°				
9:20			1		160°	
9:26			1	167°	120°	1
9:40			1	167°	120°	2
9:45			1	176°	100°	3 vibrations
9:50			1			4
11:45	#2		1		85°	
11:55		230°	2	226°	150°	
12:05 p.m.			2	215°	135°	1
12:10			2	215°	135°	2
12:15			2	185°	125°	
12.20			2		115°	3 vibrations
12:25			2			4
1:00		260°				
2:40			3	240°	125°	
2:57			3	185°	110°	
3:00		250°	3			1
3:20			3			2 vibrations
3:30			3		135°	
			Final			

NOTES

1. Temp., of stock pile taken approx. 6" deep into pile.
2. Each pass of roller consisted of 2 rolls across surface
3. 6% mixture brown in color.

TEMPERATURES

Monday, December 18, 1978

a.m.				p.m.			
1	56	7	52	1	59	7	60
2	56	8	52	2	61	8	60
3	56	9	53	3	64	9	58
4	56	10	53	4	65	10	57
5	55	11	55	5	64	11	55
8	53	Noon	57	6	62	Midnight	54

Tuesday, December 19, 1978

a.m.				p.m.			
1	57	7	57	1	65	7	64
2	57	8	58	2	66	8	62
3	57	9	59	3	67	9	58
4	56	10	61	4	69	10	55
5	56	11	63	5	69	11	54
6	57	Noon	65	6	65	Midnight	53

TABLE 12. CONSTRUCTION LOG BY SECTIONS (CONT'D)

SECTION # 4
FORMULATION NO. Asphalt
BATCH TIME 10:02 a.m.
BATCH TEMP. UNKNOWN °F

DATE December 19, 1978
PERCENT OF MIXTURE 4-1/2%
THICKNESS 3"
NO. OF LIFTS 2

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO.OF ROLLER PASSES	NOTES
10:30 a.m.	#1	330°					
10:45	#2		1	225°	125°		1. Air temperature 65° F
11.45	#3	320°	2	220°	160°		
12:30		275°		175°	125°		

SECTION # 5
FORMULATION NO. 233
BATCH TIME 7:36 a.m.
BATCH TEMP 260° F

DATE December 19, 1978
PERCENT OF MIXTURE 8%
THICKNESS 3"
NO. OF LIFTS 2

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO.OF ROLLER PASSES	NOTES
9:15 a.m.	#1						
9:20		275°					
9:30			1	245°	195°		
9:33			1			1	
10:00			1			2 vibrator	
10:10		250°	2	235°	170°	1	
10:40			2	170°	126°	2 vibrator	

SECTION # 8
FORMULATION NO. 233
BATCH TIME 6:52 a.m. to 6:59 a.m.
BATCH TEMP. 275 to 280° F

DATE December 19, 1978
PERCENT OF MIXTURE 6%
THICKNESS 3"
NO. OF LIFTS 2

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO.OF ROLLER PASSES	NOTES
8:00 a.m.	#1						
8:19		265 to 275°	1	175°	130°		
8:20			1			1	
8:30			1			2 vibrator	
8:50	265°	1	192°	140°			
9:00	#2		2	255°	190°	1	
9:05			2	245°	185°	2 vibrator	
9:20			2	165°	150°		
9:37			2		145°		
10:05			2		100°		

SECTION # 10
FORMULATION NO 230
BATCH TIME 7:32 a.m. to 7.45 a.m.
BATCH TEMP. 265 to 270° F

DATE December 18, 1978
PERCENT OF MIXTURE 6%
THICKNESS 3"
NO OF LIFTS 1

TIME	DUMPED TRUCK	STOCKPILE TEMP °F	LIFT NO	INSIDE LIFT TEMP °F	LIFT SURFACE TEMP °F	NO.OF ROLLER PASSES	
4:35 p.m	Left over		1	155°	106°		
4 50			1			1 vibrator	1 Material laid was left over from Section 3
5 10			1		100	2 vibrator	

TABLE 12. CONSTRUCTION LOG BY SECTIONS (CONT'D)

SECTION # 11
FORMULATION NO. 126
BATCH TIME 11:08 to 11:20
BATCH TEMP 260° F

DATE December 18, 1978
PERCENT OF MIXTURE 8%
THICKNESS 3"
NO. OF LIFTS 1

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO. OF ROLLER PASSES	NOTES
4:05 p.m	Left over		1	200°	150°		
4 35			1			1	1. Material laid was left over from Section 2

SECTION # 12
FORMULATION NO. 126
BATCH TIME 11:31 a.m.
BATCH TEMP 270° F

DATE
PERCENT OF MIXTURE 6%
THICKNESS 3"
NO. OF LIFTS 2

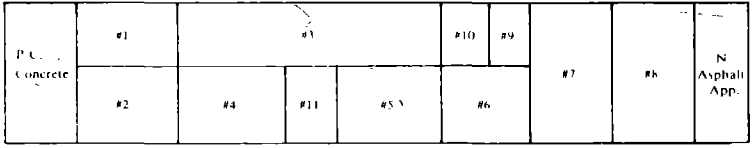
TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO. OF ROLLER PASSES	NOTES
1 35 p.m	#1	275°	1 West	250°	180°		1. Temp. of stockpile taken approx. 6" deep into pile. 2. Each pass of roller consists of 2 rolls across surface.
1:50			1 West	210°	160°	1	
1 55			1 West	210°	160°	2 vibrator	
2 00		270°					
2:05			1 West		100°		
2.05			1 East		120°	1	
2:15			1 East		120°	2 vibrator	
3 40		230°					
3 45			2 West	200°	130°		
3.55				200°		1	
4:00			2 West			2 vibrator	
4 00			1 East		150°		

SECTION # 13
FORMULATION NO. 230
BATCH TIME 7:57 a.m.
BATCH TEMP 280° F

DATE
PERCENT OF MIXTURE 8%
THICKNESS 3"
NO. OF LIFTS 2

TIME	DUMPED TRUCK	STOCKPILE TEMP. °F	LIFT NO.	INSIDE LIFT TEMP. °F	LIFT SURFACE TEMP. °F	NO. OF ROLLER PASSES	NOTES
10 00 a.m.	#1	257°					1. Temp. of stockpile taken approx. 6" deep into pile. 2. Each pass of roller consisted of 2 rollers across surface. 3. 8% mixture-black in color. 4. When loader was put on 1st lift, had no marking or tracking. 5. 8% seems to stick to equipment more than 6%.
10 05			1 West	185°	125°	1	
10:10			1 West	185°	100°	2 vibrator	
10 13		222°					
10:15			1 West	201°	100°		
10:20			1 West	201°	88°		
10.25			1 East	222°	104°		
10 30			1 East			1	
10:35			1 West.		88°		
10:45			1 West		68°		
10:45			2 West	176°	125°		
10.55		280°	2 West			1	
11 00			2 West	208°	120°		
			1 East	95°			
11:05			2 East			2 vibrator	
11 10			2 West	212°	115°		
11 25			2 West	212°	115°		
11 30			2 West			1	
11 35			2 West		108°	2 vibrator	
11 40			2 complete			3 rolled complete mat	

TABLE 13. SUMMATION OF SURFACE CHARACTERISTICS ON THE SULPHLEX ROAD TEST SECTIONS JANUARY 1980



SECTION LOCATION

	Nov '79 Benklemen Deflection	Data Provided by Texas Hwy. Dept.		Average of 2 Cores January 1980			Jan 1980 Marshall	Resilient Modulus 1979 Data	Smoothness 1980	Sand Patch 1980
		Dyna-Flect Deflection	Skid Trailer SN	Length (in.)	Density	Voids (%)				
Concrete-BWP*	.003	.003	—	8	150	3	—	—	26	.023
#1, 8% #126 BWP	.014	012	—							
#1, 8% #126 RWP**	.027	—	—	6	145	6.5	—	5×10^6	23	.019
#2, 6% #230 BWP	.015	.009	—							
#2, 6% #230 RWP	.021	—	—	7	139	10.5	—	2.9×10^6	27	.060
#3, 5% Asphalt BWP	.048	.023	—							
#3, 5% Asphalt RWP	.045	—	38	3 2	143	7	1500 at 14	$.9\times10^6$	3	.015
#4, 8% #233 BWP	.047	.026	—							
#4, 8% #233 RWP	.070	—	39	3.6	146	6	2736 at 16	3×10^6	4	019
#5, 6% #233 BWP	.047	.030	—							
#5, 6% #233 RWP	.092	—	38	3	141	8	1500 at 10	2×10^6	10	.040
#6, 8% #126 BWP	.045	036	—							
#6, 8% #126 RWP	.045	—	50	2.5	144	7	1584 at 12	5×10^6	27	025
#7, 6% #126 BWP	033	.024	—							
#7, 6% #126 RWP	.035	—	47	3	138	11	1280 at 14	2.2×10^6	110	.034
#8, 8% #230 BWP	.062	.031	—							
#8, 8% 230 RWP	.115	—	41	2.9	137	12	2736 at 20	2.7×10^6	105	.076
#9, 6% #230 BWP	.058	.038	—							
#9, 6% #230 RWP	.075	—	37	0.7	133	14	Broke	2.9×10^6	210	100
#10, 8% #230 BWP	.060	.038	—							
#10, 8% #230 RWP	.075	—	37	0.7	133	14	Broke	2.9×10^6	228	.100
#11, 6% #233 BWP	.030	033	—							
#11, 6% #233 RWP	.090	—	41	3.1	144	7	1504 at 16	2×10^6	5	025
N Asp Approach BWP	—	.033	—							
N Asp Approach RWP	—	—	—	3	143	7	—	—	280	.034
Lab Park Lot-West	—	.029	—	—	—		—			
Lab Park Lot-East	—	—	—	3	144	7	2260 at 11	—		.019

---

* Between wheel paths

** Right Wheel path

APPENDIX B (TASK H)
SPECIFICATIONS

In preparing specifications for SULPHLEX, a number of considerations must be borne in mind. The starting materials are available from multiple sources, some of the chemicals are available in ranging purities, and some of the chemicals are subject to degradation due to oxidation or polymerization, which could affect their reactivity.

Technical grade sulfur is routinely available as 99% + purity, and the source, whether Frasch or recovered, is unimportant. Localized sources of sulfur of purity less than the technical grade are available, such as surface deposits or by-product sulfur. Should such sources be considered for use, the major consideration should be the nature of the impurities. Inert filler such as gypsum, limestone, or sand should not cause a problem if present in relatively small quantities, whereas antimony, arsenic, or selenium, even in small quantities could present a potential environmental problem. Relatively large quantities of inert filler or clay could present significant problems with the viscosity or wetting capability of the resultant material. For example, too many fines from the inert filler or impurity may significantly increase the percentage binder required for a mix.

The chemicals to be considered will be limited to those modifiers used in the preparation of formulation numbers 126, 230, and 233 because these were the ones used in the experimental road construction, and the ones using the more readily available chemicals.

Coal tar describes a large number of materials. Coal tars that are unprocessed can contain light ends (volatile products) and water. These impurities can cause boiling and foaming in the reactor, so care must be exercised in the manufacture of SULPHLEX when such materials are used. The roofing grade coal tars, while more expensive, did not offer any problems when used in formulation No. 126 for the roadway. In order to establish the acceptability of any particular coal tar product, each product should be investigated singly to ensure that it would perform in the formulation in a desirable fashion.

Dicyclopentadiene has been available from two sources. One supplier has it available as a 97% pure compound, and the second supplier furnished it at a 95% purity. In the early stages of this program, both suppliers also offered an impure grade of dicyclopentadiene that was approximately 50% dicyclopentadiene. No observable differences were detected between the 97% and 95% purity products when SULPHLEX was prepared using these relatively pure materials.

In order to significantly reduce costs, the impure grade of dicyclopentadiene was investigated. Because these impure grades are essentially the drip streams or by-product from ethylene manufacture, they can vary from batch to batch, as well as from one supplier to the next. By the time the experimental roadway was to be built, only one supplier had the impure grade commercially available. This product could be partially substituted for the pure dicyclopentadiene. Recent events, however, have eliminated this material for future consideration because the supplier is closing down the refinery, which means the dicyclopentadiene will also no longer be available from this source.

Another supplier has just recently come on stream with dicyclopentadiene, and they are offering a 95% purity product. This material should perform satisfactorily, but tests should be conducted to verify this.

Although future research should be directed to using the impure grades because of the improved economics, any near-term work should limit the dicyclopentadiene to the 95% + grade.

Dipentene is available from several sources. Throughout this program the technical grade of approximately 70% from a single source has been used. The limited availability of a higher purity dipentene precluded investigating that material. Future efforts should be directed to evaluating products from different sources. Although no major property improvements are envisioned from such an effort, reduced odor or other fringe benefits could result. The fact that other terpene resins can potentially replace dipentene, dipentene products of less than 70% may also prove adequate.

Vinyl toluene is produced by two sources, although one is by far the major supplier. It is available from this major source as a 99% + purity. Vinyl toluene is inhibited with tert-butylcatechol to prevent premature polymerization. Materials stored for long periods of time, particularly during elevated summer temperatures, could affect performance. Storage should be practiced in accordance with the manufacturer's recommendation.

The manufacture and quality control of SULPHLEX is an area that needs to be fully explored. From the laboratory experiments conducted on small 200 g batches, as well as the experience gained from the 7500 pound (3400 Kg) batches prepared for the experimental roadway, some general guidelines can be established. These have been reinforced by a very limited number of experiments conducted in a pilot-scale reactor recently completed by SwRI.

Based on this experience, the preferred procedure is to add the modifiers to sulfur at 300° F (149° C) and to maintain the reaction temperature as close to 300° F (149° C) as practical. The reaction of the modifiers with sulfur is exothermic and therefore the chemicals have been added in a step-wise manner to keep the temperature from excessively exceeding the 300° F (149° C) limit. In the laboratory-size batches, if catalyzed, the reaction appeared complete within 30 minutes to 1 hour. In the large open vats used to prepare the material for the roadway, eight hours were required to add the chemicals in a step-wise manner, with the maximum temperature not exceeding 315° F (158° C).

Until recently, penetration and softening point data were used as the principal quality control specifications. With the manufacture of large quantities and storage of larger quantities, however, it has definitely been established that there is a change in penetration values with time. Viscosity measurements are currently being investigated and thus far appear to be a more consistent control than penetration, but additional study is required. The softening point has also been observed to change with time. As a result, at the present time there is no reliable performance method to distinguish one formulation from another unless a series of tests are performed as a function of time to establish this change in penetration and softening point. A review of Figures 4 and 5 will illustrate this property change with time.

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